

(19) World Intellectual Property Organization  
International Bureau(43) International Publication Date  
14 November 2002 (14.11.2002)

PCT

(10) International Publication Number  
WO 02/090481 A1(51) International Patent Classification<sup>7</sup>: C11D 3/50, 17/04

(21) International Application Number: PCT/US02/13812

(22) International Filing Date: 1 May 2002 (01.05.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
60/288,767 4 May 2001 (04.05.2001) US  
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(81) Designated States (national): AE, AG, AL, AM, AT (utility model), AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ (utility model), CZ, DE (utility model), DE, DK (utility model), DK, DM, DZ, EC, EE (utility model), EE, ES, FI (utility model), FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK (utility model), SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

## Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 02/090481 A1

(54) Title: COMPOSITIONS AND ARTICLES FOR EFFECTIVE DEPOSITION OF PERFUME

(57) Abstract: Compositions and articles are described that will rapidly dispense a unitized amount of one or more selected fabric care agents to a wash and/or rinse bath solution during the laundering process under a variety of conditions such that the fabric care additive is effectively deposited on the fabrics. Specifically, the compositions and articles made therefrom include a hydratable material, preferably effervescing materials, perfume particles and optional materials. The perfume particles are perfume combined with an inorganic carrier, preferably zeolite particles having a minimum surface area. The deposition of the perfume particles on fabrics during washing and/or rinsing provides a controlled release of the perfume components from the treated fabrics for up to two or more weeks. Also provided is a method for improving the retention of the perfume on the carrier when dispensed in an aqueous solution.

**COMPOSITIONS AND ARTICLES  
FOR EFFECTIVE DEPOSITION OF PERFUME**

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**CROSS REFERENCE TO RELATED APPLICATIONS**

20 This application claims priority under 35 U.S.C. § 119(e) to U. S. Provisional Applications Serial Nos. 60/288,767, filed May 4, 2001 (Attorney Docket No. 8541P) and 60/352,808, filed January 30, 2002 (Attorney Docket No. 8541P2).

**BACKGROUND OF THE INVENTION**

**I. Field of the Invention**

25 The present invention relates to compositions, articles and methods for supplying fabric care additives to fabrics during a laundering operation. The invention further relates to compositions and articles that will rapidly dispense a unitized amount of one or more selected fabric care agents to a wash and/or rinse bath solution during the laundering process under a variety of conditions such that the fabric care additive is 30 effectively deposited on the fabrics. More specifically, the invention relates to compositions and articles that will provide a controlled release of perfume compositions

from dry fabrics that have been treated with solutions containing the compositions, thereby providing an enduring fragrance. The field of the present invention further relates to processing aspects of combining the perfume materials with a carrier for subsequent deposition on fabrics during a laundering process and the selection of preferred carriers.

5      **II.      Description of the Prior Art**

Most consumers have come to expect scented laundry products and to expect that fabrics which have been laundered also to have a pleasing fragrance. Perfume additives make laundry compositions more aesthetically pleasing to the consumer, and in some cases the perfume imparts a pleasant fragrance to fabrics treated therewith. However, the 10 amount of perfume carryover from an aqueous laundry bath onto fabrics is often marginal. Industry has long searched for an effective perfume delivery system for use in laundry products that provides a long-lasting, storage-stable fragrance to the product, as well as effective deposition of fragrance on laundered fabrics.

Laundry and other fabric care compositions that contain perfume mixed with or 15 sprayed onto the compositions are well known from commercial practice. Because perfumes are made of a combination of volatile compounds, perfume can be continuously emitted from simple solutions and dry mixes to which the perfume has been added. Various techniques have been developed to hinder or delay the release of perfume from such compositions so that they will remain aesthetically pleasing for a longer length of 20 time. To date, however, few of the methods deliver significant fabric odor benefits after prolonged storage of the fabric.

There has been a continuing search for methods and compositions that will effectively and efficiently deliver perfume from a laundry bath onto fabric surfaces. As 25 can be seen from the following disclosures, various methods of perfume delivery have been developed involving protection of the perfume through the wash cycle, with release of the perfume onto fabrics. U.S. Pat. No. 4,096,072, Brock, et al, issued Jun. 20, 1978, teaches the use of a fatty quaternary ammonium salt to retain perfume through the wash. U.S. Pat. No. 4,402,856, Schnoring, et al, issued Sep. 6, 1983, teaches a micro-encapsulation technique that involves the formation of a shell material that allows the 30 transmission of perfume out only at certain temperatures. U.S. Pat. No. 5,066,419, Walley, et al, issued Nov. 19, 1991, teaches a perfume dispersed with a water-insoluble

nonpolymeric carrier material and encapsulated in a protective shell by a coating of water-insoluble friable material. U.S. Pat. No. 5,094,761, Trinh, et al, issued Mar. 10, 1992, teaches a perfume/cyclodextrin complex protected by clay that provides perfume benefits to at least partially wetted fabrics.

5 Further, perfume can be adsorbed onto porous carrier materials such as the polymer materials described in U.K. Pat. Pub. 2,066,839, Bares, et al, published Jul. 15, 1981. Perfumes have also been adsorbed onto a clay or zeolite material that is then admixed into particulate detergent compositions. U.S. Pat. No. 4,539,135, Ramachandran, et al, issued Sep. 3, 1985, discloses particulate laundry compounds comprising a clay or 10 zeolite material carrying perfume. U.S. Pat. No. 4,713,193, Tai, issued Dec. 15, 1987, discloses a free-flowing particulate detergent additive comprising a liquid or oily adjunct with a zeolite material. Japanese Patent HEI 4[1992]-218583, Nishishiro, published Aug. 10, 1992, discloses controlled-release materials including perfumes plus zeolites. U.S. Pat. No. 4,304,675, Corey, et al, issued Dec. 8, 1981, teaches a method and composition 15 comprising zeolites for deodorizing articles.

Combinations of perfumes generally with larger pore size zeolites such as zeolite X and Y are also taught in the art. East German Patent Publication No. 248,508, published Aug. 12, 1987 relates to perfume dispensers (e.g., an air freshener) containing a faujasite-type zeolite (e.g., zeolite X and Y) loaded with perfume. The critical molecular 20 diameters of the perfume molecules are said to be between 2-8 Angstroms. Also, East German Patent Publication No. 137,599, published Sep. 12, 1979 teaches compositions for use in powdered washing agents to provide thermoregulated release of perfume. Zeolites A, X and Y are taught for use in these compositions. These earlier teachings are repeated in the more recently filed European applications Publication No. 535,942, 25 published Apr. 7, 1993, and Publication No. 536,942, published Apr. 14, 1993, by Unilever PLC. More recently, these teachings have been repeated in U.S. Pat. No. 5,336,665, issued Aug. 9, 1994 to Garner-Gray, et al. and in U.S. Patent No. 5,955,419, issued Sept. 21, 1999 to Barket, Jr., et al.

30 Forming articles from compositions that comprise perfume and inorganic carriers are also known generally in the art. WO 99/21953, published May 6, 1999, Henkel, discloses a method for producing aromatic beads with bulk densities greater than 700 g/l,

wherein a solid, water-free premix comprised of carrier(s), auxiliary agent(s), and perfume is subjected to granulation or compacted agglomeration and WO 99/45091, published Sept. 10. 1999, Henkel, discloses highly dosed fragrant compounds with apparent densities of more than 700 g/l that are produced by granulation or pressure 5 agglomeration and mixed with other powder-form and/or granular detergent constituents.

While tablets with a variety of perfume carriers are commercially available, they have several disadvantages not the least of which include strength or robustness and solubility. It is possible to prepare fast dissolving tablets by incorporating materials in fine powder or particulate form of less than about 40 microns in diameter. However, tablet formulations that are designed to meet short cycle time solubility criteria, especially in cold water below about 10°C, in laundry washing and/or rinsing process, have poor strength and are frequently damaged during transport. In order to compensate for the presence of the smaller particle sized materials, excessive amounts of binder must be added which commonly gives rise to solubility issues. Thus, there is an unresolved need for a tablet that meets desired strength and solubility criteria, and is able to incorporate a large percentage a fine powdered perfume carrier or other particular materials while ensuring the stability of the article from its preparation to the end use.

Effervescent systems and materials have been incorporated into such compositions and articles in order to obtain improved dissolution characteristics, particularly under cold water conditions. However, the use of effervescent components and other hydratable materials in such compositions and articles further heightens their sensitivity to atmospheric moisture or humidity. U.S. Pat. No. 5,993,854, issued Nov. 30, 1999, Needleman, et al., discloses an aroma releasing composition that comprises an effervescent agent, an exothermic agent and a volatile agent, the effervescent and exothermic agents being provided in a ratio sufficient to promote release of the volatile agent, when the composition is placed in water. U.S. Pat. No. 5,997,901, issued Dec. 7, 1999, Mills, discloses a scented molded product that is made by mixing sodium bicarbonate, water and fragrance oils to form a first mixture, adding to this first mixture a citric acid mixture comprising sodium borate mixed with citric acid to form a third mixture and molding and drying the third mixture to form a hardened product. WO 93/08255, published April 29, 1993, Kruse, et al., discloses the use of sorbite as a carrier

in combination with carbonate and acid are used as a gas evolving system in fragrance beads. Further, U.S.S.N. 09/838,863 filed April 20, 2001 by Caswell, et al. discloses effervescent articles that comprise one or more fabric actives including perfume.

While the adsorption of perfume onto zeolite or polymeric carriers may perhaps provide some improvement over the addition of neat perfume admixed with detergent compositions, the industry is still searching for improvements in the length of storage time of the laundry compositions without loss of perfume characteristics such as intensity, the amount of fragrance delivered to fabrics, and perhaps most importantly in the duration of the perfume scent on the treated fabric surfaces. As is described in additional detail below, the release of perfume from a zeolite carrier material is a moisture activated release. A complicating factor in the use of such materials is the pre-mature release of perfume components early during the laundering process. The present invention provides for improved retention of the perfume in the zeolite such that more perfume is retained on fabric through the laundering process to be released from the dry fabric in the presence of atmospheric moisture or humidity.

Another problem in providing perfumed laundry products is the balance between the odor intensity of the perfume on treated dry fabric and the intensity of the odor intensity of the laundry composition itself. Therefore, a need still exists for a perfume delivery system which substantially releases the perfume odor during use and thereafter from the dry fabric, but which does not provide an overly intensive odor to the product itself.

The present invention solves the long-standing need for a simple, effective, storage-stable delivery system that provides benefits, especially a long lasting dry fabric odor benefit, after the laundering process. Further, the perfume-containing compositions of the present invention have reduced product odor during storage. The present invention also provides the additional benefit of continued odor release from laundered fabrics when exposed to humidity while being stored, dried or ironed, providing an enduring fragrance.

#### SUMMARY OF THE INVENTION

A perfume delivery composition is provided that comprises a hydrating material, perfume particles and optional components such as binders, free perfumes, colorants and

supplemental disintegrants. The hydrating material is between about 0% and about 90%, preferably between about 30% and about 60% and more preferably between about 50% and about 60% by weight of the delivery composition. The perfume particles comprise a carrier particle and a perfume composition and constitute between about 1% and about 5 40% by weight of the delivery composition. The delivery composition of the present invention is further characterized in that at least about 30%, preferably at least about 40% and more preferably at least about 50% by volume of the components are in the form of fine powders or particulates having a mean particle size of less than about 100 microns, and preferably less than about 40 microns. The fine particle size is an important 10 characteristic to balance efficient deposition of the desired fabric care technology versus ensuring no visible residues on fabric.

In a process aspect of the present invention, a method of entrapping perfume in an inorganic porous particle comprises the steps of contacting the carrier particles with a perfume composition, mixing the carrier and perfume, allowing heat to be generated as 15 the perfume enters the carrier pores and then cooling the mixture. A hydrating material and optional binder material can be added to the entrapped perfume particles to prepare the compositions of the present invention.

The present invention further provides for a temperature and humidity stable unit dose perfume delivery article that comprises a perfume composition, a material selected 20 from a perfume carrier, preferably zeolite, a hydrating material and mixtures thereof, and a humidity resistant package, wherein at least about 30%, preferably at least about 40% and more preferably at least about 50% by volume of the components are in the form of fine powders or particulates having a mean particle size of less than about 100 microns, and preferably less than about 40 microns. The articles of the present invention have 25 sufficient hardness to survive handling and transportation, will rapidly dissolve in water less than about 10°C during a short cycle washing and/or rinsing process without leaving residue, and will deposit perfume components onto the fabric and provide for a slow release of those components when exposed to atmospheric moisture. The long-term stability of such articles is insured by packaging the articles with materials that provide a 30 moisture barrier, expressed as a moisture vapor transmission rate (MVTR), of at less than

about 1.2 g H<sub>2</sub>O/day/m<sup>2</sup>, preferably less than about 0.1 g H<sub>2</sub>O/day/m<sup>2</sup>, and more preferably less than about 0.02 g H<sub>2</sub>O/day/m<sup>2</sup>.

In a further process aspect of the present invention, a process for making tablets that have at least about 30%, preferably at least about 40% and more preferably at least 5 about 50% by volume of the components are in the form of fine powders or particulates having a mean particle size of less than about 100 microns, and preferably less than about 40 microns, is provided. The tablets are preferably made through the compression of a powder mixture of the composition into various sizes and shapes including generally, 10 cylindrical, elliptical, square, polygon, spherical and others. A binder material is preferably added to promote tablet formation and tablet stability. The tablets may be formed on most low pressure tableting machines available in the industry without hardness or solubility issues.

Further, the present invention provides an effervescent article for dispensing in a laundry wash and/or rinse bath solution, the article having a perfume or mixture of 15 perfumes that is between about 1% and about 50% by weight, and an effervescent system comprising an acid source, a carbon dioxide source and an optional binder. Optionally, the effervescent system will comprise an effervescent granule to improve the release of the perfume(s) from the effervescent article.

The present invention further relates to zeolites for use in providing effective 20 deposition on fabrics, improved perfume retention through a laundering operation, and controlled release of the perfume from the dry treated fabric over a prolonged period. The zeolite particles can be any zeolite having a mean surface area of at least about 475 m<sup>2</sup>/g, preferably greater than about 525 m<sup>2</sup>/g, and more preferably at least about 580 m<sup>2</sup>/g. The zeolite is preferably a type X zeolite having the described surface area 25 characteristics, and is more preferably Zeolite 13X.

The present invention further relates to the use of the compositions and articles of the present invention to deliver to a given laundry solution, a unitized dose of a selected perfume composition to customize that laundry solution and the perfume deposited on the fabrics laundered in that solution.

30 In a further process aspect, the invention provides methods for dispensing packaged compositions/articles of the present invention for use by individuals in

5 customizing a laundry solution to deliver a perfume composition selected by the individual. The method also includes the step of providing a dispensing device for housing the supply of packaged compositions/articles that is capable of allowing an individual to select one or more compositions/articles and removing the packaged composition/article from the dispensing device.

10 The present invention also provides a merchandising display for use in a retail environment that comprises a supply of the compositions and/or articles of the present invention. The display of the present invention further comprises information to assist the consumer in selecting a composition and/or article for use in combination with a detergent, a fabric softener or other fabric care article to achieve one or more fabric care 15 benefits desired by the consumer. Optionally, the display may include a computer or other interactive means to assist the consumer in selecting a composition and/or article.

15 All percentages, ratios and proportions herein are by weight, unless otherwise specified. All temperatures are in degrees Celsius (°C) unless otherwise specified. All documents cited are, in relevant part, incorporated herein by reference.

#### **DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS**

20 The present invention concerns compositions and articles that will deliver perfume to fabrics in a laundry solution, regardless of whether the solution is a wash and/or rinse bath solution, the temperature of the solution or the presence of other materials in the 25 solution. Further, methods for preparing such compositions and articles as well as various methods of use are also described herein below.

##### **I. Perfume Delivery Composition Having Hydrating Material**

25 The present invention relates to a stable perfume delivery composition for use in delivering a perfume composition to fabrics, preferably by dispensing the composition in the laundry wash and/or rinse bath solutions. The compositions of the present invention comprise a hydrating material, perfume particles and one or more optional components, wherein at least about 30%, preferably at least about 40% and more preferably at least about 50% by volume, of the components have a mean particle size of less than about 100 micrometers and even more preferably less than about 40 micrometers.

30 **A. Hydratable Material**

For purposes of the present invention "hydrating material" refers to a material or combination of materials that undergo a physical and/or chemical change in the presence of water or moisture. A common characteristic of hydrating materials is the ability to easily wet or hydrate in the presence of water. Non-limiting examples of such materials 5 are water-soluble salts, polymers, starches, and surfactants. Other preferred hydrating materials are materials that react with one another in the presence of water. Effervescent materials are good examples of this latter group of hydrating materials that are especially preferred since they ensure fast dissolution and act to disperse fine powder materials in the wash liquor.

10 For cold water solubility, the compositions of the present invention will contain highly water soluble materials. Disintegrants described hereinafter that are activated in the presence of water may also be used to advantage as hydrating materials in the articles of the present invention.

### 1. Effervescent Components

15 The use of effervescent systems not only provides a preferred method for formulating the articles of the present invention, but also provides very rapid disintegration and dissolution of the article after it is dispensed in the laundry solution. A simplified effervescent system will comprise an acid and carbon dioxide source material that will react in the presence of water to produce carbon dioxide. The generation of 20 carbon dioxide within the composition, and more particularly within articles made from the composition, causes the article to rapidly disintegrate and release the active or mixture of actives to the laundry solution. As is described in additional detail below, this disintegration and active release may be improved by increasing the rate of reaction between the acid and carbon dioxide source material. Effervescent systems are 25 particularly useful in promoting rapid dissolution of tablets and capsules under cold water conditions, e.g. less than about 30°C, preferably less than about 20°C and more preferably less than about 10°C.

30 A laundry article containing an effervescent system is a preferred embodiment of the present invention. While the effervescent systems for use in the present invention are described hereinafter in terms of an acid and carbon dioxide source material that generate carbon dioxide in the presence of water, the effervescent systems useful herein may

comprise any material or combination of materials that will generate a gas when dispensed in an aqueous laundry solution.

The articles of the present invention preferably have an effervescent system or components that comprise an acid source and a carbon dioxide source. It is important to consider two criteria for the effervescent system, namely (1) the stability of the composition/article during handling, transport, and storage, and (2) the rate of solubility when contacted with water. There are two important physical properties that control the two criteria mentioned, specifically, (1) the surface area available for hydration, and (2) the contact area between the effervescent composition materials.

10 The surface area available for hydration can be controlled by varying particle size. However, while stability increases as particle sizes increase, particle dissolution rates decrease as particle sizes increase. Particle stability may also be increased by restricting the penetration of water from the contact interface of the acid and carbon dioxide source. However, faster dissolution rates are obtained by maximizing the penetration of water at the contact interface of the acid and carbon dioxide source. Hence, one must compromise to achieve an effervescent composition that meets both desired stability and solubility criteria.

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Achieving the right effervescent system is a function of the particle size of the system and contact between the individual components. The particle size of the system defines the total surface area available for hydration. The particle sizes of the individual components define the contact area at the interface of the acid and carbon dioxide source and the ratio of these particle sizes can be used as a measure of that contact area. More specifically, it has been found that a high ratio of acid particle size to carbon dioxide particle size results in increased article stability. More preferably, the ratio of acid:carbon dioxide source is sufficiently high that the carbon dioxide source "coats" the acid source so as to form a hydration layer upon moisture penetration. This hydration layer acts to restrict further penetration of water vapor e.g. humidity, into the particle, thereby preventing the effervescing of the particle, and thus increasing the stability of the effervescent system. A particle size ratio of acid to carbon dioxide source materials of more than about 5:1, preferably more than about 20:1, and more preferably greater than about 60:1 is desired for high particle stability.

A faster dissolution rate for an effervescent system can be achieved by preventing complete "coating" of the acid source by the carbon dioxide source, i.e. a lower contact area between the acid source and the carbon dioxide source. A lower contact area can be achieved by forming an intimate mixture of acid and carbon dioxide source materials that 5 have a particle size ratio of acid to carbon dioxide source of about 6:1, more preferably about 3:1, most preferably about 1:1.

In the preferred embodiment of the invention, a particle size ratio of acid to carbon dioxide source material of about 7:1, and preferably of about 5:1 provides a balance between stability and solubility of the effervescent system.

10 It is also preferred that the acid source and the carbon dioxide source are intimately mixed with one another, preferably in an effervescent granule. These effervescent granules may then be used to prepare solid articles of the present invention in the form of tablets, spheres, bars and most any moldable shape. The composition and manufacture of an effervescent granule is described below.

15 a) Acid

Suitable acid sources for use in the compositions of the present invention include those materials that are capable of providing solid organic, mineral or inorganic acids, preferably in the form of acids, salts, derivatives thereof or mixtures thereof. Preferred derivatives include esters of such acids.

20 The organic acids are preferred, and will include mono-, bi- or tri-protonic acids. Such preferred acids include mono- or polycarboxylic acids preferably citric acid, adipic acid, glutaric acid, 3 cetoglutaric acid, citramalic acid, tartaric acid, maleic acid, fumaric acid, maleic acid, succinic acid, malonic acid. Such acids can be used in their acidic or anhydrous forms or mixtures thereof. Other preferred acids include sulphonic acids such 25 as toluenesulphonic acid. Surprisingly, it has now been found that by using citric acid, tartaric acid, maleic acid and/ or malic acid, improved physical and/or chemical stability over prolonged storage periods may be achieved. Furthermore, it has been found that these materials, and in particular tartaric acid, exhibit improved dissolution characteristics resulting in an improved effervescence performance.

30 The acid source, and preferably the acid itself, is a particulate compound whereof at least about 75%, preferably at least about 85%, more preferably at least about 90%,

even more preferably at least about 95% and further still preferably at least about 99% by volume, has a particle size from about 0.1 to about 1180 microns, and preferably from about 300 to about 700 microns. The particle size of the acid source and the carbon dioxide source material described hereinafter, can be determined by any method known in the art, but in particular may be determined by laser light scattering or defraction technique, such as is used in the Malvern 2600 or Sympatec Helos laser light scattering equipment (or deflectometer).

5 The particulate acid source is preferably obtained by grinding or milling coarse acid source material, shortly before it is combined with the carbonate source described 10 hereinafter. Specifically, it is advantageous to store the acid source material in a coarse form and grind the material immediately prior to its use to avoid problems that accompany the storage of finely ground acid materials.

15 b) Carbon Dioxide Source Material

An effervescent system used in the compositions of the present invention would 20 further comprises a carbon dioxide source. As used herein, "carbon dioxide source" includes any material that can provide carbon dioxide when reacting with an acid upon contact with water. The carbon dioxide source material includes carbonates, bicarbonates, percarbonate salts and mixtures thereof, however, bicarbonates and/or carbonates are preferred.

Suitable carbonates to be used herein include carbonate and hydrogen carbonate of potassium, lithium, sodium, and the like, amongst which sodium and potassium carbonate are preferred. Suitable bicarbonates to be used herein include any alkali metal salt of bicarbonate like lithium, sodium, potassium and the like, amongst which sodium and potassium bicarbonate are preferred. Bicarbonate may be preferred in combination 25 with or as an alternative to carbonate, because it is more weight effective. However, the choice of carbonate or bicarbonate or mixtures thereof in the dry effervescent granules described hereinafter may be made depending on the pH desired in the aqueous medium wherein the dry effervescent granules are dissolved. For example, in an aqueous wash solution where a relative high pH is desired (e.g., above about pH 9.5) it may be preferred 30 to use carbonate alone or to use a combination of carbonate and bicarbonate wherein the level of carbonate is higher than the level of bicarbonate, typically in a weight ratio of

carbonate to bicarbonate from about 0.1 to about 10, more preferably from about 1 to about 5 and most preferably from about 1 to about 2.

The carbon dioxide source has a volume median particle size from about 0.1 to about 200 microns, wherein at least about 60%, preferably at least about 70% more preferably at least about 80%, and even more preferably at least about 90% by volume has a particle size of between about 5 to about 100 microns. It is however, preferred that the carbon dioxide source have a mean particle size that is smaller than the mean particle size of the acid source. Likewise, a carbon dioxide source having a desired particle size may be obtained by grinding a larger particle size material, optionally followed by selecting the material with the required particle size by any suitable separation method. It is preferred that the carbon dioxide source material have a mean particle size that is less than about 100 microns, more preferably less than about 38 microns and even more preferably less than about 10 microns.

The particle size of the carbon dioxide source material used plays a critical role in rate of dissolution. The use of a fine particulate carbon dioxide source to "coat" a larger particulate acid source results in an improved dissolution profile, especially when the acid source and carbon dioxide source are combined with other ingredients to form a compressed tablet. This improved dissolution profile is preferred where the article is required to dissolve in water that is less than about 30°C, preferably less than about 20°C, more preferably less than about 10°C, and even more preferably between about 7° and about 10°C.

#### EXAMPLE 1

##### *Effect of Size Ratio on Dissolution Rates*

Two batches of tablets are prepared using granular citric acid having a mean particle diameter of about 500 microns. In one batch, about 55g of citric acid is coated with about 45g of a first carbon dioxide source material having a mean particle diameter of less than about 38 microns, while in the second batch, about 55g citric acid is coated with about 45g carbon dioxide source material having a mean particle diameter of about 300 microns. Each powder is compressed into a cylindrical tablet using a force of about 15 kN. The tablets containing the first carbon dioxide source materials exhibit a strength value of about 85 Newtons and the tablets containing the second carbon dioxide source

exhibit a strength value of about 80 Newtons. When dispensed into about 200g water at a temperature of about 20°C, the tablets containing the smaller carbon dioxide source material dissolve in about 25 seconds while the larger carbon dioxide source material dissolve in about 46 seconds.

5                   c) Effervescent granule

The acid and carbon dioxide source, or at least part thereof are preferably present in an intimate mixture with one another, which means the acid source and carbon dioxide source are homogeneously mixed. Thus, in one preferred embodiment, a portion of the acid and a portion of the carbon dioxide source are not separate discrete particles. The 10 intimate mixing should result in the acid and the carbon dioxide source being formed into a preferably dry effervescence granule. By "dry" it is to be understood that the granule is substantially free of water, i.e., that no water has been added or present other than the moisture of the raw materials themselves, as free moisture or in a hydrated form. Typically, the level of water is below about 5% by weight of the total intimate mixture or 15 granule, preferably below about 3% and more preferably below about 1.5%.

The acid is preferably present in the intimate mixture or the effervescent granules at a level of from about 0.1% to about 99% by weight of the total granule, preferably from about 30% to about 95%, more preferably from about 45% to about 85% and even more preferably from about 50% to about 80%. The carbon dioxide source is preferably present in the intimate mixture or the effervescent granules at a level of from about 0.1% to about 99% by weight of the total, preferably from about 3% to about 75%, more preferably from about 5% to about 60%, and even more preferably from about 15% to about 50%.

It may be preferred that an optional desiccant be present in the intimate mixture of 25 the effervescence granule, such as oven dried inorganic and organic salts, anhydrous salts, oven dried silicates and alumino-silicates, anhydrous silicates and/ or sulphate salts.

For optimum effervescence in an aqueous medium the weight ratio of acid to carbon dioxide source in the intimate mixture or the effervescent granule is preferably from about 0.05 to about 3, more preferably from about 0.1 to about 1.5, and even more 30 preferably from about 0.2 to about 1. An especially preferred weight ratio of acid to

carbon dioxide source material in the intimate mixture or the effervescent granule for rapid dissolution in water at less than about 10°C is about 1.2.

The effervescent granules are obtainable by a process comprising a granulation step, and preferably comprising the step of dry-powder compaction or pressure 5 agglomeration. While all binding mechanisms can occur in pressure agglomeration, adhesion forces between the solid particles, i.e., between the acid, carbon dioxide source and optionally the binder if present, play an especially important role. This is because pressure agglomeration, especially high pressure agglomeration, is an essentially dry process that forms new entities (i.e., dry effervescent granules) from solid particles (i.e., 10 the acid, bicarbonate, carbonate source and optionally the binder) by applying external forces to densify a more or less defined bulk mass or volume, creating binding mechanisms between the solid particles that provide strength to the new entity, i.e. the high external force applied brings the solid particles closer together. The inventors have 15 surprisingly found that in the present invention reduced pressure may be sufficient to form a stable granule incorporating the small particle size acid source, with preferably small particle size carbon dioxide source as defined above.

The effervescent granules may have any particle size, the preferred particle size depending on the application and the components of the granule. For instance, it has been found that effervescent granules having (a) a weight average particle size of from about 20 500 microns to about 1500 microns wherein at least about 70% by weight of said granule has a particle size from about 350 to about 2000 microns, preferably (b) having a weight average particle size from about 650 microns to about 1180 microns wherein at least about 70% by weight of said granule has a particle size from about 500 to about 1500 microns, or more preferably (c) having a weight average particle size from about 710 25 microns to about 1000 microns wherein at least about 70% by weight of said granule has a particle size from about 600 to about 1180 microns, can provide improved dispensing/dissolution.

Similarly, it has been found that effervescent particles (d) of a weight average particle size from about 200 microns to about 500 microns wherein at least about 70% of 30 said granule has a particle size from about 100 to about 710 microns, and preferably (e) having a weight average particle size from about 250 microns to about 450 microns

wherein at least about 70% of said granule has a particle size of from about 150 to about 650 microns, can provide better dispensing and/or dissolution of the composition than larger effervescent particles.

The weight average particle size of the effervescent granule herein can be 5 determined by any method known in the art, in particular by sieving a sample of the particulate acid through a series of sieves, typically five, with meshes of various diameter or aperture size, obtaining a number of fractions (thus having a particle size of above, below or between the mesh sizes of the used sieve sizes), whereof the weight is determined (weight fractions). The average particle size per fraction and then the weight 10 average particle size of the material can be calculated, taking in account the weight percentage per fraction (e.g. plotting the weight fractions against the aperture size of the sieves).

It may be preferred that the effervescence system optionally comprise a coating 15 agent, which can be selected from any coating agent known in the art. Preferred coating agents are materials that can be applied to the granule in the form of a melt, which is solid under ambient conditions. Such coating agents will include polymeric materials and nonionic surfactants. Also preferred may be coating agents that can be applied to the granules in the form of an aqueous solution or a solution in an organic solvent, including 20 organic and inorganic acids or salts. Furthermore, the effervescent granules may be dusted with a particulate material such as a desiccant to coat the granules.

d) Process For Making Effervescent Component

A process for manufacturing the effervescent component for use in the articles of the present invention preferably comprises the steps of: (a) first obtaining the acid source 25 of the particle size defined herein, preferably by grinding larger particle size acid source material as commercially available; (b) mixing the thus obtained acid source with the carbon dioxide source, preferably by grinding larger particle size carbon dioxide source material as commercially available, and optionally mixing a binder and/or other ingredients, to form a mixture; and (c) submitting the mixture to a granulation step, 30 preferably comprising the step of extrusion, spheronisation, more preferably compaction or agglomeration. Optionally, other ingredients can be added to the obtained granule, such as coating agents.

By "granulation step" it is meant that the resulting mixture is made into granules of the required size as defined herein before. A preferred process to be used herein is roller compaction. In this process the acid and carbon dioxide sources and optionally the binder and other ingredients, after having been mixed together, are forced between two 5 compaction rollers that apply a pressure to said mixture so that the rotation of the rolls transforms the mixture into a compacted sheet/flake. This compacted sheet/flake is then granulated. One way to carry this out is to mill the compacted flake/sheet or to granulate the agglomerate mixture by conventional means. Milling may typically be carried out with a Flake Crusher FC 200® commercially available from Hosokawa Bepex GmbH. 10 Depending on the end particle size desired for the effervescent granules the milled material may further be sieved. Sieving of the dry effervescent granules can for example be carried out with a commercially available Alpine Airjet Screen®.

According to this process the effervescent raw materials and optionally the binder if present are preferably mixed together without the addition of water and/or moisture 15 apart those coming from the raw materials themselves so as to obtain a dry free flowing powder mixture. This dry free flowing powder mixture comprising the effervescent particles (i.e. the acid and carbon dioxide source), and optionally the binder particles if present, undergoes a granulation step, preferably a pressure agglomeration step, i.e. a dry process step wherein this free flowing powder mixture undergoes high external forces that 20 bring the particles closely together thereby densifying the bulk mass of said particles to create binding mechanisms between the solid effervescent particles and the binder if present.

Typical roller compactors for use herein is for example Pharmapaktor L200/50P® 25 commercially available from Hosokawa Bepex GmbH. The process variables during the pressure agglomeration step via roller compaction are the distance between the rolls, the feed rate, the compaction pressure and the roll speed. The typical feeding device is a feed screw. The distance between the rolls is typically from about 0.5 cm to about 10 cm, preferably from about 3 to about 7 cm, more preferably from about 4 to about 6 cm. The pressing force is typically between about 20 kN and about 120 kN, preferably from about 30 kN to about 100 kN, and more preferably from about 40 kN to about 80 kN, although lower pressures are possible and may be preferred when employing fine particle size acid 30

sources. Typically, the roll speed is between about 1 rpm and about 180 rpm, preferably from about 2 rpm to about 50 rpm and more preferably from about 2 rpm to about 35 rpm. Typically, the feed rate is between about 1 rpm and about 100 rpm, preferably from about 5 rpm to about 70 rpm, more preferably from about 8 rpm to about 50 rpm.

5 Temperature at which compaction is carried out is not relevant, typically it varies from about 0° C to about 40 °C. It may be preferred that the granules are made under dry-air, having a humidity of below about 30%.

10 Dissolution studies comparing non-compacted acid source/carbon dioxide source raw materials with raw materials compacted with a roller compactor as described above, reveal that the compacted raw materials give faster dissolution rates.

#### EXAMPLE 2

##### *Dissolution Rates – Compacted vs. Non-Compacted Raw Materials*

In preparing the compacted raw materials, about 55g of citric acid having a mean particle size of about 600 microns and about 45g of sodium carbonate having a mean 15 particle size of about 90 microns are compacted into a sheet employing a Bepex K50/200 compactor with 5 RPM roll speed and about 80 kN compaction force with about 4 mm nip gap between rolls. The sheet is ground using a Bepex FC200, to collect particles of less than about 1000 microns. The granular powder is compressed into a cylindrical tablet using a compressive force 15kN. In the preparation of the non-compacted raw 20 materials, about 55g of citric acid having a mean particle size of about 600 microns and about 45g of sodium carbonate having a mean particle size of about 90 micrometers are mixed using a drum mixer. This powder is compressed into a cylindrical tablet using a compressive force of about 15 kN. The tablets made with the compacted raw materials give an average strength value of about 194 Newtons, and an average dissolution time of 25 about 265 seconds. The tablets made with non-compacted materials have an average strength value of about 108 Newtons, and an average dissolution time of about 329 seconds. Compression of the powder yields a tablet of high strength and the compaction of the effervescent raw materials provide intimate contact between the acid source and the carbon dioxide source that give faster dissolution rates.

30 2. Other Hydrating Materials

Non-effervescent hydrating materials including water-soluble cellular matrices, starch, water swellable and super absorbent polymers, organic and inorganic highly soluble salts, and the like, all may be used to advantage in compositions and articles of the present invention. The criteria for selecting such hydrating materials is that in the 5 presence of water the hydrating material is activated to cause an article of the present invention to break apart, thereby promoting the dissolution of the article. Preferably, such hydrating materials will not leave residue in the laundry solution that might otherwise deposit on fabrics in the solution.

Water-soluble cellular matrix perfume microcapsules are solid particles containing 10 perfume stably held in the cells. The water-soluble matrix material comprises mainly polysaccharide and polyhydroxy compounds. The polysaccharides are preferably higher polysaccharides of the non-sweet, colloidally-soluble types, such as natural gums, e.g., gum arabic, starch derivatives, dextrinized and hydrolyzed starches, and the like. The polyhydroxy compounds are preferably alcohols, plant-type sugars, lactones, monoethers, 15 and acetals. The cellular matrix microcapsules useful in the present invention are prepared by, e.g., (1) forming an aqueous phase of the polysaccharide and polyhydroxy compound in proper proportions, with added emulsifier if necessary or desirable; (2) emulsifying the perfumes in the aqueous phase; and (3) removing moisture while the mass is plastic or flowable, e.g., by spray drying droplets of the emulsion. The matrix 20 materials and process details are disclosed in, e.g., U.S. Pat. No. 3,971,852, Brenner, et al., issued July 27, 1976, which is incorporated herein by reference. Moisture-activated perfume microcapsules of the cellular type can be obtained commercially, e.g., as IN-CAP® from Polak's Frutal Works, Inc., Middletown, New York; and as Optilok System® 25 encapsulated perfumes from Encapsulated Technology, Inc., Nyack, New York.

Alternatively, crude starch matrix perfume particles can be prepared according to 25 the disclosure in U.S. Pat. No. 5,267,531. Perfume oil is first emulsified with various starches and water for a period of two hours. The emulsion is then spray dried and checked for proper oil content.

## B. Perfume Particles

30 1. Perfume Composition  
a) Perfume Actives

The perfume compositions useful in the perfume delivery compositions and articles of the present invention comprise between about 1% and about 50%, but preferably greater than about 3% and more preferably greater than about 5% by weight of the composition of a perfume active of mixture of perfume actives.

5 As used herein the term "perfume" is used to indicate any odoriferous material that is subsequently released into the aqueous bath and/or onto fabrics contacted therewith. The perfume will most often be liquid at ambient temperatures. A wide variety of chemicals are known for perfume uses, including materials such as aldehydes, ketones, and esters. More commonly, naturally occurring plant and animal oils and 10 exudates comprising complex mixtures of various chemical components are known for use as perfumes. The perfumes herein can be relatively simple in their compositions or can comprise highly sophisticated complex mixtures of natural and synthetic chemical components, all chosen to provide any desired odor. Typical perfumes can comprise, for example, woody/earthy bases containing exotic materials such as sandalwood, civet and 15 patchouli oil. The perfumes can be of a light floral fragrance, e.g. rose extract, violet extract, and lilac. The perfumes can also be formulated to provide desirable fruity odors, e.g. lime, lemon, and orange. Further, it is anticipated that so-called "designer fragrances" that are typically applied directly to the skin will be used when desired by the consumer. Likewise, the perfumes delivered in the compositions and articles of the 20 present invention may be selected for an aromatherapy effect, such as providing a relaxing or invigorating mood. As such, any material that exudes a pleasant or otherwise desirable odor can be used as a perfume active in the compositions and articles of the present invention.

Preferably, at least about 25%, more preferably at least about 50%, even more 25 preferably at least about 75%, by weight of the perfume is composed of fragrance material selected from the group consisting of aromatic and aliphatic esters having molecular weights from about 130 to about 250; aliphatic and aromatic alcohols having molecular weights from about 90 to about 240; aliphatic ketones having molecular weights from about 150 to about 260; aromatic ketones having molecular weights from 30 about 150 to about 270; aromatic and aliphatic lactones having molecular weights from about 130 to about 290; aliphatic aldehydes having molecular weights from about 140 to

about 200; aromatic aldehydes having molecular weights from about 90 to about 230; aliphatic and aromatic ethers having molecular weights from about 150 to about 270; and condensation products of aldehydes and amines having molecular weights from about 180 to about 320; and essentially free from nitromusks and halogenated fragrance materials.

5 More preferably, at least about 25%, more preferably at least about 50%, most preferably at least about 75%, by weight of the perfume is composed of fragrance material selected from the group consisting of:

Common Name	Chemical Type	Chemical Name	Approx.M.W.
Adoxal	aliphatic aldehyde	2,6,10-trimethyl-9-undecen-1-al	210
allyl amyl glycolate	Ester	allyl amyl glycolate	182
allyl cyclohexane propionate	Ester	allyl-3-cyclohexyl propionate	196
Amyl acetate	Ester	3-methyl-1-butanol acetate	130
Amyl salicylate	Ester	amyl salicylate	208
anisic aldehyde	aromatic aldehyde	4-methoxy benzaldehyde	136
Aurantiol	schiff base	condensation product of methyl anthranilate and hydroxycitronellal	305
Bacdanol	aliphatic alcohol	2-ethyl-4-(2,2,3-trimethyl-3-cyclopenten-1-yl)-2-buten-1-ol	208
benzaldehyde	aromatic aldehyde	benzaldehyde	106
benzophenone	aromatic ketone	benzophenone	182
benzyl acetate	Ester	benzyl acetate	150
benzyl salicylate	Ester	benzyl salicylate	228

beta damascone	aliphatic ketone	1-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2-buten-1-one	192
beta gamma hexanol	Alcohol	3-hexen-1-ol	100
Buccoxime	aliphatic ketone	1,5-dimethyl-oxime bicyclo[3,2,1] octan-8-one	167
Cedrol	Alcohol	octahydro-3,6,8,8-tetramethyl-1H-3A,7-methanoazulen-6-ol	222
Cetalox	Ether	dodecahydro-3A,6,6,9A-tetramethylnaphtho[2,1B]-furan	236
cis-3-hexenyl acetate	Ester	cis-3-hexenyl acetate	142
cis-3-hexenyl salicylate	Ester	beta, gamma-hexenyl salicylate	220
Citronellol	Alcohol	3,7-dimethyl-6-octenol	156
citronellyl nitrile	Nitrile	geranyl nitrile	151
clove stem oil	Natural		
Coumarin	Lactone	coumarin	146
cyclohexyl salicylate	Ester	cyclohexyl salicylate	220
Cymal	aromatic aldehyde	2-methyl-3-(para iso propyl phenyl)propionaldehyde	190
decyl aldehyde	aliphatic aldehyde	decyl aldehyde	156
delta damascone	aliphatic ketone	1-(2,6,6-trimethyl-3-cyclohexen-1-yl)-2-buten-1-one	192
dihydromyrcenol	Alcohol	3-methylene-7-methyl octan-7-ol	156
dimethyl benzyl carbinal acetate	Ester	dimethyl benzyl carbinal acetate	192

ethyl vanillin	aromatic aldehyde	ethyl vanillin	166
ethyl-2-methyl butyrate	Ester	ethyl-2-methyl butyrate	130
ethylene brassylate	macrocyclic lactone	ethylene tridecan-1,13-dioate	270
Eucalyptol	aliphatic epoxide	1,8-epoxy-para-menthane	154
Eugenol	Alcohol	4-allyl-2-methoxy phenol	164
Exaltolide	macrocyclic lactone	cyclopentadecanolide	240
flor acetate	Ester	dihydro-nor-cyclopentadienyl acetate	190
Florhydral	aromatic aldehyde	3-(3-isopropylphenyl)butanal	190
Frutene	Ester	dihydro-nor-cyclopentadienyl propionate	206
Galaxolide	Ether	1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopentagamma-2-benzopyrane	258
gamma decalactone	Lactone	4-N-hepty-4-hydroxybutanoic acid lactone	170
gamma dodecalactone	Lactone	4-N-octyl-4-hydroxybutanoic acid lactone	198
Geraniol	Alcohol	3,7-dimethyl-2,6-octadien-1-ol	154
geranyl acetate	Ester	3,7-dimethyl-2,6-octadien-1-yl acetate	196

geranyl nitrile	Ester	3,7-diemthyl-2,6-octadienenitrile	149
Helional	aromatic aldehyde	alpha-methyl-3,4,(methylenedioxy)hydrocinnamaldehyde	192
Heliotropin	aromatic aldehyde	heliotropin	150
hexyl acetate	Ester	hexyl acetate	144
hexyl cinnamic aldehyde	aromatic aldehyde	alpha-n-hexyl cinnamic aldehyde	216
hexyl salicylate	Ester	hexyl salicylate	222
hydroxyambran	aliphatic alcohol	2-cyclododecyl-propanol	226
hydroxycitronellal	aliphatic aldehydye	hydroxycitronellal	172
ionone alpha	aliphatic ketone	4-(2,6,6-trimethyl-1-cyclohexenyl-1-yl)-3-buten-2-one	192
ionone beta	aliphatic ketone	4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3-butene-2-one	192
ionone gamma methyl	aliphatic ketone	4-(2,6,6-trimethyl-2-cyclohexyl-1-yl)-3-methyl-3-buten-2-one	206
iso E super	aliphatic ketone	7-acetyl-1,2,3,4,5,6,7,8-octahydro-1,1,6,7,tetramethyl naphthalene	234
iso eugenol	Ether	2-methoxy-4-(1-propenyl)phenol	164

iso jasmone	aliphatic ketone	2-methyl-3-(2-pentenyl)-2-cyclopenten-1-one	166
Koavone	aliphatic aldehyde	acetyl di-isoamylene	182
lauric aldehyde	aliphatic aldehyde	lauric aldehyde	184
Lavandin	Natural		
Lavender	Natural		
lemon CP	Natural	major component d-limonene	
d-limonene/orange terpenes	Alkene	1-methyl-4-iso-propenyl-1-cyclohexene	136
Linalool	Alcohol	3-hydroxy-3,7-dimethyl-1,6-octadiene	154
linalyl acetate	Ester	3-hydroxy-3,7-dimethyl-1,6-octadiene acetate	196
lrg 201	Ester	2,4-dihydroxy-3,6-dimethyl benzoic acid methyl ester	196
Lyral	aliphatic aldehyde	4-(4-hydroxy-4-methylpentyl) 3-cyclohexene-1-carboxaldehyde	210
Majantol	aliphatic alcohol	2,2-dimethyl-3-(3-methylphenyl)-propanol	178
Mayol	Alcohol	4-(1-methylethyl) cyclohexane methanol	156
methyl anthranilate	aromatic amine	methyl-2-aminobenzoate	151
methyl beta naphthyl ketone	aromatic ketone	methyl beta naphthyl ketone	170

methyl cedrylone	aliphatic ketone	methyl cedrenyl ketone	246
methyl chavicol	Ester	1-methyloxy-4,2-propen-1-yl benzene	148
methyl dihydro jasmonate	aliphatic ketone	methyl dihydro jasmonate	226
methyl nonyl acetaldehyde	aliphatic aldehyde	methyl nonyl acetaldehyde	184
musk indanone	aromatic ketone	4-acetyl-6-tert butyl-1,1-dimethyl indane	244
Nerol	Alcohol	2-cis-3,7-dimethyl-2,6-octadien-1-ol	154
Nonalactone	Lactone	4-hydroxynonanoic acid, lactone	156
Norlimbanol	aliphatic alcohol	1-(2,2,6-trimethyl-cyclohexyl)-3-hexanol	226
orange CP	Natural	major component d-limonene	
P. T. bucinal	aromatic aldehyde	2-methyl-3(para tert butylphenyl) propionaldehyde	204
para hydroxy phenyl butanone	aromatic ketone	para hydroxy phenyl butanone	164
Patchouli	Natural		
phenyl acetaldehyde	aromatic aldehyde	1-oxo-2-phenylethane	120
phenyl acetaldehyde dimethyl acetal	aromatic aldehyde	phenyl acetaldehyde dimethyl acetal	166
phenyl ethyl acetate	Ester	phenyl ethyl acetate	164
phenyl ethyl alcohol	Alcohol	phenyl ethyl alcohol	122

phenyl ethyl phenyl acetate	Ester	2-phenylethyl phenyl acetate	240
phenyl hexanol/phenoxanol	Alcohol	3-methyl-5-phenylpentanol	178
Polysantol	aliphatic alcohol	3,3-dimethyl-5-(2,2,3-trimethyl-3-cyclopenten-1-yl)-4-penten-2-ol	221
prenyl acetate	Ester	2-methylbuten-2-ol-4-acetate	128
Rosaphen	aromatic alcohol	2-methyl-5-phenyl pentanol	178
Sandalwood	Natural		
alpha-terpinene	aliphatic alkane	1-methyl-4-iso-propylcyclohexadiene-1,3	136
terpineol (alpha terpineol and beta terpineol)	Alcohol	para-menth-1-en-8-ol, para-menth-1-en-1-ol	154
terpinyl acetate	Ester	para-menth-1-en-8-yl acetate	196
tetra hydro linalool	aliphatic alcohol	3,7-dimethyl-3-octanol	158
tetrahydromyrcenol	aliphatic alcohol	2,6-dimethyl-2-octanol	158
tonalid/musk plus	aromatic ketone	7-acetyl-1,1,3,4,4,6-hexamethyl tetralin	258
undecalactone	Lactone	4-N-heptyl-4-hydroxybutanoic acid lactone	184
Undecavertol	Alcohol	4-methyl-3-decen-5-ol	170
undecyl aldehyde	aliphatic aldehyde	undecanal	170

undecylenic aldehyde	aliphatic aldehyde	undecylenic aldehyde	168
Vanillin	aromatic aldehyde	4-hydroxy-3-methoxybenzaldehyde	152
Verdox	Ester	2-tert-butyl cyclohexyl acetate	198
Vertenex	Ester	4-tert-butyl cyclohexyl acetate	198

and mixtures thereof.

The compositions and articles of manufacture of the present invention can optionally comprises free perfume. During the laundry process, when perfume is not incorporated in a perfume carrier, a substantial amount of that free perfume that is added to the wash and/or the rinse cycle is lost with the water and in the subsequent drying cycle (either line drying or machine drying). This has resulted in both a waste of unusable perfume that are not deposited on the laundered fabrics, and a contribution to the general air pollution from the release of volatile organic compounds to the air. It is therefore preferable that at least about 25%, more preferably at least about 50%, even more preferably at least about 75%, by weight of the free perfume is composed of enduring perfume ingredients. These enduring perfume ingredients are characterized by their boiling points (B.P.) and their ClogP value. The enduring perfume ingredients of this invention have a B.P. measured at the normal, standard pressure of 760 mm Hg, of about 240°C or higher, preferably of about 250°C or higher, and a ClogP of about 2.7 or higher, preferably of about 2.9 or higher, and even more preferably of about 3.0 or higher. The enduring perfume ingredients tend to be substantive and remain on fabric after the laundry washing and drying process.

As described in U.S. Pat. No. 5,500,138, issued Mar. 19, 1996 to Bacon and Trinh, incorporated herein by reference, the ClogP of an active is a reference to the "calculated" octanol/water partitioning coefficient of the active and serves as a measure of the hydrophobicity of the active. The ClogP of an active can be calculated according to the methods quoted in "The Hydrophobic Fragmental Constant" R.F. Rekker, Elsevier, Oxford or Chem. Rev, Vol. 71, No. 5, 1971, C. Hansch and A.I. Leo, or by using a ClogP

program from Daylight Chemical Information Systems, Inc. Such a program also lists experimental logP values when they are available in the Pomona92 database. The "calculated logP" (ClogP) can be determined by the fragment approach of Hansch and Leo (cf., A. Leo in *Comprehensive Medicinal Chemistry*, Vol. 4, C. Hansch, P.G. 5 Sammens, J.B. Taylor, and C.A. Ramsden, Eds. p 295, Pergamon Press, 1990). The fragment approach is based on the chemical structure of each compound and takes into account the numbers and types of atoms, the atom connectivity, and chemical bonding.

The boiling points of many perfume ingredients are given in, e.g., "Perfume and Flavor Chemicals (Aroma Chemicals)," Steffen Arctander, published by the author, 1969, 10 incorporated herein by reference. Other boiling point values can be obtained from different chemistry handbooks and data bases, such as the Beilstein Handbook, Lange's Handbook of Chemistry, and the CRC Handbook of Chemistry and Physics. When a boiling point is given only at a different pressure, usually lower pressure than the normal pressure of 760 mm Hg, the boiling point at normal pressure can be approximately 15 estimated by using boiling point-pressure nomographs, such as those given in "The Chemist's Companion," A. J. Gordon and R. A. Ford, John Wiley & Sons Publishers, 1972, pp. 30-36. The boiling point values can also be estimated via a computer program that is described in "Development of a Quantitative Structure - Property Relationship Model for Estimating Normal Boiling Points of Small Multifunctional Organic 20 Molecules", David T. Stanton, *Journal of Chemical Information and Computer Sciences*, Vol. 40, No. 1, 2000, pp. 81-90.

Thus, when a perfume composition which is composed of enduring perfume ingredients, as well as when other organic actives of the present invention, have a B. P. of about 250°C or higher, and a ClogP of about 3.0 or higher, they are very effectively 25 deposited on fabrics, and remain substantive on fabrics after the rinsing and drying (line or machine drying) steps.

Nonlimiting examples of the preferred enduring perfume ingredients of the present invention include: benzyl salicylate, adoxal, allyl cyclohexane propionate (allyl-3-cyclohexyl propionate), alpha damascone, ambrettolide (trade name for 30 oxacycloheptadec-10-en-2-one), ambretone (trade name for 5-cyclohexadecen-1-one), ambroxan, amyl cinnamic aldehyde, amyl cinnamic aldehyde dimethyl acetal, amyl

salicylate, ambrinol 20t (trade name for 2,5,5-trimethyl-octahydro-2-naphthol), iso E super (trade name for 7-acetyl-1,2,3,4,5,6,7,8-octahydro-1,1,6,7,tetramethylnaphthalene), anandol (trade name for 2-ethyl-4-(2,2,3-trimethyl-3-cyclopenten-1-yl)-2-buten-1-ol), aurantiol (trade name for hydroxycitronellal-methyl anthranilate), benzyl benzoate, 5 nirvanol (trade name for 4-penten-2-ol,3,3-dimethyl-5-(2,2,3 trimethyl-3-cyclopenten-1-yl)-), undecalactone (4-N-heptyl-4-hydroxybutanoic acid lactone), beta naphthol methyl ether, bourgeonal (trade name for 3-(4-tert butylphenyl)-propanal), cyclohexadecenone (cis-/trans-cyclohexadec-8-en-1-one), caryophyllene extra, methyl cedrylone (methyl cedrenyl ketone), neobutenone (trade name for 4-penten-1-one, 1-(5,5-dimethyl-1-cyclohexen-1-yl)), cedramber, cedac (trade name for cedrynyl acetate), cedrol (octahydro-3,6,8,8-tetramethyl-1H-3A,7-methanoazulen-6-ol), musk C-14 (trade name for ethylene dodecane dioate), cis-3-hexenyl salicylate, citrathal, citronellyl propionate, galaxolide (trade name for 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-gamma-2-benzopyrane), cyclohexyl salicylate, cymal (trade name for 2-methyl-3-(para iso propyl benzopyrane), damascone beta (1-(2,6,6-trimethylcyclohexen-1-yl)-2-buten-1-one), damascenone (1-(2,6,6-trimethyl-1,3-cyclohexadien-1-yl)-2-buten-1-one), delta damascone (1-(2,6,6-trimethyl-3-cyclo-hexen-1-yl)-2-buten-1-one), dihydro iso jasmonate, diphenyl methane, dupical (trade name for 4-(tricyclo(5.2.1.0 2,6)decylidene-8)-butanal), diphenyl oxide, gamma-dodecalactone, delta-dodecalactone, ethyl cinnamate, 15 ebanol, ethylene brassylate (ethylene tridecan-1,13-dioate), florhydral (trade name for 3-(3-isopropylphenyl) butanol), habanolide (trade name for oxacyclohexadec-12+13-en-2-one), hexyl cinnamic aldehyde (alpha-n-hexyl cinnamic aldehyde), hexyl salicylate, hydroxyambran (trade name for 2-cyclododecyl-propanol), ionone alpha (4-(2,6,6-trimethyl-1-cyclohexenyl-1-yl)-3-buten-2-one), ionone beta (4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3-butene-2-one), ionone gamma methyl (4-(2,6,6-trimethyl-2-cyclohexyl-1-yl)-3-methyl-3-buten-2-one), ionone methyl, iralia, iso butyl quinoline, lauric aldehyde, p. t. bucinal (trade name for 2-methyl-3(para tertbutylphenyl) propionaldehyde), musk ketone, musk indanone (trade name for 4-acetyl-6-tert butyl-1,1-dimethyl indane), musk plus (trade name for 7-acetyl-1,1,3,4,4,6-hexamethyl tetralin), 20 octalynol (trade name for 1-naphthalenol, 1,2,3,4,4a,5,8,8a,octahydro-2,2,6,8-tetramethyl), ozonil (trade name for tridecen-2-nitrile), phantolide (trade name for 5-tetramethyl),

acetyl-1,1,2,3,3,6-hexamethylindan), phenafleur (trade name for cyclohexyl phenyl ethyl ether), phenyl ethyl benzoate, phenyl ethyl phenyl acetate (2-phenylethyl phenyl acetate), vetiveryl acetate, sandalwood, amyl benzoate, amyl cinnamate, cadinene, cedryl acetate, cedryl formate, cinnamyl cinnamate, cyclamen aldehyde, exaltolide (trade name for 15-hydroxypentadecanoic acid, lactone), geranyl anthranilate, hexadecanolide, hexenyl salicylate, linayl benzoate, 2-methoxy naphthalene, methyl cinnamate, methyl dihydrojasmonate, beta-methyl napthyl ketone, musk tibetine, myristicin, delta-nonalactone, oxahexadecanolide-10, oxahexadecanolide-11, patchouli alcohol, phenyl heptanol, phenyl hexanol (3-methyl-5-phenylpentanol), alpha-santalol, thibetolide (trade name for 15-hydroxypentadecanoic acid, lactone), delta-undecalactone, gamma-undecalactone, yara-yara, methyl-N-methyl anthranilate, benzyl butyrate, benzyl iso valerate, citronellyl isobutyrate, delta nonalactone, dimethyl benzyl carbonyl acetate, dodecanal, geranyl acetate, geranyl isobutyrate, gamma-ionone, para-isopropyl phenylacetaldehyde, tonalid (trade name for 7-acetyl-1,1,3,4,4,6-hexamethyl tetralin), iso-amyl salicylate, ethyl undecylenate, benzophenone, beta-caryophyllene, dodecalactone, lilial (trade name for para-tertiary-butyl-alpha-methyl hydrocinnamic aldehyde), and mixtures thereof.

The preferred perfume compositions used in the present invention contain at least 5 different enduring perfume ingredients, preferably at least 6 enduring perfume ingredients, more preferably at least 7 different enduring perfume ingredients, and even more preferably at least 8 different enduring perfume ingredients. Most common perfume ingredients which are derived from natural sources, are composed of a multitude of components. When each such material is used in the formulation of the preferred perfume compositions of the present invention, it is counted as one single ingredient, for the purpose of defining the invention.

In the perfume art, some materials having no odor or very faint odor are used as diluents or extenders. Non-limiting examples of these materials are dipropylene glycol, diethyl phthalate, triethyl citrate, isopropyl myristate, and benzyl benzoate. These materials are used for, e.g., diluting and stabilizing some other perfume ingredients. These materials are not counted in the formulation of the lasting perfume compositions of the present invention.

The perfume compositions of the present invention can also comprise some low odor detection threshold perfume actives. The odor detection threshold of an odorous material is the lowest vapor concentration of that material which can be olfactorily detected. The odor detection threshold and some odor detection threshold values are 5 discussed in, e.g., "Standardized Human Olfactory Thresholds", M. Devos et al, IRL Press at Oxford University Press, 1990, and "Compilation of Odor and Taste Threshold Values Data", F. A. Fazzalari, editor, ASTM Data Series DS 48A, American Society for Testing and Materials, 1978, both of said publications being incorporated by reference. The use of small amounts of perfume ingredients that have low odor detection threshold 10 values can improve perfume odor character, even though they are not as substantive as the enduring perfume ingredients disclosed hereinabove.

Perfume ingredients having a significantly low detection threshold, useful in the lasting perfume composition of the present invention, are selected from the group consisting of allyl amyl glycolate, ambrox (trade name for 1,5,5,9-tetramethyl-1,3-oxatricyclotridecane), anethole, bacdanol (trade name for 2-ethyl-4-(2,2,3-trimethyl-3-cyclopenten-1-yl)-2-buten-1-ol), benzyl acetone, benzyl salicylate, butyl anthranilate, calone, cetalox (trade name for dodecahydro-3A,6,6,9A-tetramethylnaphtho[2,1B]-furan), cinnamic alcohol, coumarin, cyclogalbanate, Cyclal C (trade name for 3-cyclohexene-1-carboxaldehyde, 3,5-dimethyl-), cymal (trade name for 2-methyl-3-(para iso 20 propylphenyl)propionaldehyde), damascenone (trade name for 1-(2,6,6-trimethyl-1,3-cyclohexadien-1-yl)-2-buten-1-one), alpha-damascone, 4-decenal, dihydro isojasmonate, gamma-dodecalactone, ebanol, ethyl anthranilate, ethyl-2-methyl butyrate, ethyl methylphenyl glycidate, ethyl vanillin, eugenol, flor acetate (trade name for dihydro-nor-cyclopentadienyl acetate), florhydral (trade name for 3-(3-isopropylphenyl) butanol), 25 fructone (ethyl-2-methyl-1,3-dioxolane-2-acetate), frutene (dihydro-nor-cyclopentadienyl propionate), heliotropin, herbavert, cis-3-hexenyl salicylate, indole, ionone alpha, ionone beta, iso cyclo citral, isoeugenol, alpha-isomethylionone, keone, lilial (trade name for para-tertiary butyl alpha-methyl hydrocinnamic aldehyde), linalool, lyral (trade name for 4-(4-hydroxy-4-methyl-pentyl)3-cyclohexene-1-carboxaldehyde), methyl anthranilate, 30 methyl dihydrojasmonate, methyl heptine carbonate, methyl isobutetyl tetrahydropyran, methyl beta naphthyl ketone, methyl nonyl ketone, beta naphthol methyl ether, nerol,

para-anisic aldehyde, para hydroxy phenyl butanone, phenyl acetaldehyde, gamma-undecalactone, undecylenic aldehyde, vanillin, and mixtures thereof.

These low odor detection threshold materials are preferably present at low levels in addition to the enduring perfume ingredients, typically less than about 20%, preferably less than about 15%, more preferably less than about 10%, by weight of the total perfume compositions of the present invention. It is understood that these materials can be used at levels higher than 20% and even up to 100% of the total perfume composition. Some enduring perfume ingredients also have low odor detection threshold. These materials are counted as enduring perfume ingredients in the formulation of the perfume compositions of the present invention

The following non-limiting examples exemplify enduring perfume compositions:

## Enduring Perfume A

	<u>Perfume Ingredients</u>	<u>Wt. %</u>
15	Benzyl Salicylate	10
	Coumarin	5
	Ethyl Vanillin	2
	Ethylene Brassyate	10
20	Galaxolide	15
	Hexyl Cinnamic Aldehyde	20
	Gamma Methyl Ionone	10
	Lilial	15
	Methyl Dihydrojasmonate	5
25	Patchouli	5
	Tonalid	<u>3</u>
	Total	100

### Enduring Perfume B

## Perfume Ingredients

	Vertinex (4 - tertiary butyl cyclohexyl acetate)	3
	Methyl cedrylone	2
	Verdox	3
	Galaxolide	14
5	Tonalid	5
	Hexyl salicylate	4
	Benzyl salicylate	4
	Hexyl cinnamic aldehyde	6
	P. T. Bucinal	6
10	Musk indanone	7
	Ambrettolide	2
	Sandela	5
	Phentolide	2
	Vetivert acetate	4
15	Patchouli	2
	Geranyl phenylacetate	6
	Okoumal	6
	Citronellyl acetate	3
	Citronellol	5
20	Phenyl ethyl alcohol	5
	Ethyl vanillin	2
	Coumarin	1
	Flor acetate	1
	Linalool	<u>2</u>
25	Total	100

Perfume absorbed onto and/or into a porous carrier such as zeolite to form perfumed particles is another approach to reduce the perfume release and/or perfume loss. When the perfume is to be adsorbed onto zeolite, the perfume raw materials or mixtures of perfume raw materials may be selected according to the description provided in U.S. Pat. No. 5,955,419 issued Sept. 21, 1999, to Barket, Jr., et al., which is incorporated

herein by reference. Also preferred are perfumes carried through the laundry process and thereafter released into the air around the dried fabrics (e.g. such as the space around the fabric during storage). This requires movement of the perfume out of the zeolite pores with subsequent partitioning into the air around the fabric. Preferred perfume agents are therefore further identified on the basis of their volatility. Boiling point is used herein as a measure of volatility and preferred materials have a boiling point less than about 300°C. Perfume actives and mixtures of actives useful for the present invention preferably comprise at least about 50% of deliverable actives with boiling points less than 300°C (preferably at least about 60%; more preferably at least about 70% of such actives). In addition, in the perfume actives that are preferred for use in the compositions and articles of the present invention will have at least about 80%, and more preferably at least about 90%, of the deliverable actives have a "ClogP value" greater than about 1.0. The ClogP value for an active or mixture of actives may be obtained as described below.

#### Stable and Unstable Perfume Ingredients

It is now discovered that surprisingly, many common perfume ingredients are not compatible with porous mineral carrier materials, such as clays and zeolites, particularly dehydrated/activated zeolites. It is found that some perfume ingredients are degraded upon incorporation into a porous mineral carrier material, forming materials that are undesirable and/or not intended in the original perfume compositions. Furthermore, some of these ingredients can cause discoloration in some compositions.

An unstable perfume ingredient can be identified by loading a liquid perfume composition comprising at least 6 perfume ingredients including the perfume ingredient being studied into a sample of activated/dehydrated zeolite 13X, according to the procedure given hereinbelow, and stored under anhydrous condition for about 24 hours. The perfume ingredients are then extracted with acetone to be recovered as free perfume and analyzed by gas chromatography to determine its stability. A perfume ingredient is characterized as an "unstable perfume ingredient" if at least about 50% of that ingredient, preferably at least 65%, more preferably at least about 80%, and even more preferably at least about 95% of that ingredient is decomposed into other by-products, and not recovered from the extraction.

Non-limiting examples of the unstable perfume ingredients that are not suitable for use in the present invention preferably include ingredients selected from the group consisting of allylic alcohol ester, secondary alcohol ester, tertiary alcohol ester, allylic ketone, condensation product of amines and aldehydes, and mixtures thereof, and more 5 preferably include ingredients selected from the group consisting of allylic alcohol ester, secondary alcohol ester, tertiary alcohol ester, allylic ketone, acetal, ketal, condensation product of amines and aldehydes, and mixtures thereof.

“Allylic alcohol” refers to an alcohol molecule wherein the carbon atom carrying the alcoholic hydroxyl group is covalently bonded to a carbon-carbon double bond in the 10 alpha and beta positions, namely, having the general structure  $C(OH)-C=C$ . Non-limiting examples of allylic alcohol ester perfume ingredients include allyl amyl glycolate, allyl anthranilate, allyl benzoate, allyl butyrate, allyl caprate, allyl caproate, allyl cinnamate, allyl cyclohexane acetate, allyl cyclohexane butyrate, allyl cyclohexane propionate, allyl heptoate, allyl nonanoate, allyl salicylate, amyl cinnamyl acetate, amyl cinnamyl formate, 15 cinnamyl formate, cinnamyl acetate, cyclogalbanate, geranyl acetate, geranyl acetoacetate, geranyl benzoate, geranyl cinnamate, methallyl butyrate, methallyl caproate, neryl acetate, neryl butyrate, amyl cinnamyl formate, alpha-methyl cinnamyl acetate, methyl geranyl tiglate, mertenyl acetate, farnesyl acetate, fenchyl acetate, geranyl anthranilate, geranyl butyrate, geranyl iso-butyrate, geranyl caproate, geranyl caprylate, geranyl ethyl 20 carbonate, geranyl formate, geranyl furoate, geranyl heptoate, geranyl methoxy acetate, geranyl pelargonate, geranyl phenylacetate, geranyl phthalate, geranyl propionate, geranyl iso-propoxyacetate, geranyl valerate, geranyl iso-valerate, trans-2-hexenyl acetate, trans-2-hexenyl butyrate, trans-2-hexenyl caproate, trans-2-hexenyl phenylacetate, trans-2-hexenyl propionate, trans-2-hexenyl tiglate, trans-2-hexenyl valerate, beta-pentenyl 25 acetate, alpha-phenyl allyl acetate, prenyl acetate, trichloromethylphenylcarbiny1 acetate, and mixtures thereof.

“Secondary alcohol” refers to an alcohol molecule wherein the carbon atom carrying the alcoholic hydroxyl group is covalently bonded to a hydrogen atom and two carbon atoms, namely, having the general structure  $C-CH(OH)-C$ . Non-limiting examples 30 of secondary alcohol ester perfume ingredients include secondary-n-amyl acetate, ortho-tertiary-amyl cyclohexyl acetate, isoamyl benzyl acetate, secondary-n-amyl butyrate, amyl

vinyl carbonyl acetate, amyl vinyl carbonyl propionate, cyclohexyl salicylate, dihydro-nor-cyclopentadienyl acetate, dihydro-nor-cyclopentadienyl propionate, isobornyl acetate, isobornyl salicylate, isobornyl valerate, flor acetate, frutene, 2-methylbuten-2-ol-4-acetate, methyl phenyl carbonyl acetate, 2-methyl-3-phenyl propan-2-yl acetate, prenyl acetate, 4-tert-butyl cyclohexyl acetate, verdox (2-tert-butyl cyclohexyl acetate), vertenex, (4-tert-butylcyclohexyl acetate), Violiff (carbonic acid 4-cycloocten-1-yl methyl ester), ethenyl-iso-amyl carbonylacetate, fenchyl acetate, fenchyl benzoate, fenchyl-n-butyrate, fenchyl isobutyrate, laevo-menthyl acetate, dl-menthyl acetate, menthyl anthranilate, menthyl benzoate, menthyl-iso-butyrate, menthyl formate, laevo-menthyl phenylacetate, menthyl propionate, menthyl salicylate, menthyl-iso-valerate, cyclohexyl acetate, cyclohexyl anthranilate, cyclohexyl benzoate, cyclohexyl butyrate, cyclohexyl-iso-butyrate, cyclohexyl caproate, cyclohexyl cinnamate, cyclohexyl formate, cyclohexyl heptoate, cyclohexyl oxalate, cyclohexyl pelargonate, cyclohexyl phenylacetate, cyclohexyl propionate, cyclohexyl thioglycolate, cyclohexyl valerate, cyclohexyl-iso-valerate, methyl amylacetate, methyl benzyl carbonyl acetate, methyl butyl cyclohexanyl acetate, 5-methyl-3-butyl-tetrahydropyran-4-yl acetate, methyl citrate, methyl-iso-campholate, 2-methyl cyclohexyl acetate, 4-methyl cyclohexyl acetate, 4-methyl cyclohexyl methyl carbonyl acetate, methyl ethyl benzyl carbonyl acetate, 2-methylheptanol-6-acetate, methyl heptenyl acetate, alpha-methyl-n-hexyl carbonyl formate, methyl-2-methylbutyrate, methyl nonyl carbonyl acetate, methyl phenyl carbonyl acetate, methyl phenyl carbonyl anthranilate, methyl phenyl carbonyl benzoate, methyl phenyl carbonyl-n-butyrate, methyl phenyl carbonyl-iso-butyrate, methyl phenyl carbonyl caproate, methyl phenyl carbonyl caprylate, methyl phenyl carbonyl cinnamate, methyl phenyl carbonyl formate, methyl phenyl carbonyl phenylacetate, methyl phenyl carbonyl propionate, methyl phenyl carbonyl salicylate, methyl phenyl carbonyl-iso-valerate, 3-nonanyl acetate, 3-nonenyl acetate, nonane diol-2:3-acetate, nonynol acetate, 2-octanyl acetate, 3-octanyl acetate, n-octyl acetate, secondary-octyl-iso-butyrate, beta-pentenyl acetate, alpha-phenyl allyl acetate, phenylethyl methyl carbonyl-iso-valerate, phenylethyleneglycol diphenylacetate, phenylethyl ethynyl carbonyl acetate, phenylglycol diacetate, secondary-phenylglycol monoacetate, phenylglycol monobenzoate, isopropyl caprate, isopropyl caproate, isopropyl caprylate, isopropyl cinnamate, para-isopropyl cyclohexanyl acetate,

propylglycol diacetate, propyleneglycol di-isobutyrate, propyleneglycol dipropionate, isopropyl-n-heptoate, isopropyl-n-hept-1-yne carbonate, isopropyl pelargonate, isopropyl propionate, isopropyl undecylenate, isopropyl-n-valerate, isopropyl-n-valerate, isopropyl-  
5 iso-valerate, isopropyl sebacinate, isopulegyl acetate, isopulegyl acetoacetate, isopulegyl isobutyrate, isopulegyl formate, thymyl propionate, alpha-2,4-trimethyl cyclohexane methylacetate, trimethyl cyclohexyl acetate, vanillin triacetate, vanillylidene diacetate, vanillyl vanillate, and mixtures thereof.

“Tertiary alcohol” refers to an alcohol molecule wherein the carbon atom carrying the alcoholic hydroxyl group is covalently bonded to three other carbon atoms, namely,  
10 having the general structure



Non-limiting examples of tertiary alcohol ester include tertiary-amyl acetate, caryophyllene acetate, cedrenyl acetate, cedryl acetate, dihydromyrcenyl acetate, dihydroterpinyl acetate, dimethyl benzyl carbinal acetate, dimethyl benzyl carbinal isobutyrate, dimethyl heptenyl acetate, dimethyl heptenyl formate, dimethyl heptenyl propionate, dimethyl heptenyl-iso-butyrate, dimethyl phenylethyl carbinal acetate, dimethyl phenylethyl carbinal-iso-butyrate, dimethyl phenylethyl carbinal-iso-valerate, dihydro-nor-dicyclopentadienyl acetate, dimethyl benzyl carbinal butyrate, dimethyl benzyl carbinal formate, dimethyl benzyl carbinal propionate, dimethyl phenylethyl carbinal-n-butyrate, dimethyl phenylethyl carbinal formate, dimethyl phenylethyl carbinal propionate, elemyl acetate, ethinyl cyclohexylacetate, eudesmyl acetate, eugenyl cinnamate, eugenyl formate, iso-eugenyl formate, eugenyl phenylacetate, isoeudehyl phenylacetate, guaiyl acetate, hydroxycitronellyl ethylcarbonate, linallyl acetate, linallyl anthranilate, linallyl benzoate, linallyl butyrate, linallyl isobutyrate, linallyl caproate, linallyl caprylate, linallyl cinnamate, linallyl citronellate, linallyl formate, linallyl heptoate, linallyl-N-methylanthranilate, linallyl methyltiglate, linallyl pelargonate, linallyl phenylacetate, linallyl propionate, linallyl pyruvate, linallyl salicylate, linallyl-n-valerate, linallyl-iso-valerate, methylcyclopentenolone butyrate, methyl cyclopentenolone propionate, methyl ethyl phenyl carbinal acetate, methyl heptin carbonate, methyl

nicotinate, myrcenyl acetate, myrcenyl formate, myrcenyl propionate, cis-ocimenyl acetate, phenyl salicylate, terpinyl acetate, terpinyl anthranilate, terpinyl benzoate, terpinyl-n-butyrate, terpinyl-iso-butyrate, terpinyl cinnamate, terpinyl formate, terpinyl phenylacetate, terpinyl propionate, terpinyl-n-valerate, terpinyl-iso-valerate, tributyl 5 acetylcitrate, and mixtures thereof.

Some alcohols of the unstable alcohol ester perfume ingredients can be both allylic and secondary, or both allylic and tertiary. Non-limiting examples of these ingredients are amyl vinyl carbonyl acetate, amyl vinyl carbonyl propionate, hexyl vinyl carbonyl acetate, 3-nonenyl acetate, 4-hydroxy-2-hexenyl acetate, linallyl anthranilate, linallyl benzoate, linallyl butyrate, linallyl isobutyrate, linallyl caproate, linallyl caprylate, linallyl 10 cinnamate, linallyl citronellate, linallyl formate, linallyl heptoate, linallyl-N-methylantranilate, linallyl methyltiglate, linallyl pelargonate, linallyl phenylacetate, linallyl propionate, linallyl pyruvate, linallyl salicylate, linallyl-n-valerate, linallyl-iso-15 valerate, myrtenyl acetate, nerolidyl acetate, nerolidyl butyrate, beta-pentenyl acetate, alpha-phenyl allyl acetate, and mixtures thereof.

“Allylic ketone” refers to a ketone molecule wherein the ketone functional group is covalently bonded to a carbon-carbon double bond in the alpha and beta positions, namely, having a general structure C-C(=O)-C=C. Non-limiting examples of allylic ketone perfume ingredients include acetyl furan, allethrolone, allyl ionone, allyl pulegone, amyl cyclopentenone, benzylidene acetone, benzylidene acetophenone, alpha iso methyl 20 ionone, 4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3-buten-2-one, beta damascone (1-(2,6,6-trimethylcyclohexen-1-yl)-2-buten-1-one), damascenone (1-(2,6,6-trimethyl-1,3-cyclohexadien-1-yl)-2-buten-1-one), delta damascone (1-(2,6,6-trimethyl-3-cyclohexen-1-yl)-2-buten-1-one), alpha ionone (4-(2,6,6-trimethyl-1-cyclohexenyl-1-yl)-3-buten-2-one), beta ionone (4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3-butene-2-one), gamma methyl 25 ionone (4-(2,6,6-trimethyl-2-cyclohexyl-1-yl)-3-methyl-3-buten-2-one), pulegone, and mixtures thereof.

“Acetal” refers to an acetal molecule wherein the aldehyde functional group is covalently bonded to two oxygen atoms of two hydroxyl groups at the same carbonyl 30 carbon, namely, having a general structure C-CH(OC)<sub>2</sub>. Non-limiting examples of acetal

perfume ingredients include acetaldehyde-benzyl-beta-methoxyethyl acetal, acetaldehyde-di-iso-amyl acetal, acetaldehyde-di-pentandiol acetal, acetaldehyde-di-n-propyl acetal, 10 acetaldehyde-ethyl-trans-3-hexenyl acetal, acetaldehyde-phenylethylene glycol acetal, acetaldehyde phenylethyl-n-propylacetal, cinnamic aldehyde dimethyl acetal, 5 acetaldehyde-benzyl-beta-methoxyethyl acetal, acetaldehyde-di-iso-amylacetal, acetaldehyde diethylacetal, acetaldehyde-di-cis-3-hexenyl acetal, acetaldehyde-di pentanediol acetal , acetaldehyde-di-n-propyl acetal, acetaldehyde-ethyl-trans-3-hexenyl acetal, acetaldehyde-phenylethylene glycol acetal, acetaldehyde phenylethyl-n-propylacetal, acetylvanillin dimethylacetal, alpha-amylcinnamic aldehyde-di-iso-propyl 10 acetal, p-tertiary-amyl phenoxy acetaldehyde diethylacetal, anisaldehyde-diethylacetal, anisaldehyde-dimethylacetal, iso-apiole, benzaldehyde diethylacetal, benzaldehyde-di- (ethyleneglycol monobutylether) acetal, benzaldehyde dimethylacetal, benzaldehyde ethyleneglycolacetal, benzaldehyde glyceryl acetal, benzaldehydepolypropylene glycol acetal, 15 cinnamic aldehyde diethyl acetal, citral diethyl acetal, citral dimethyl acetal, citral propylene glycol acetal, alpha-methylcinnamic aldehyde diethylacetal, alpha-cinnamic aldehyde dimethylacetal, phenylacetalddehyde-2,3-butyleneglycol acetal, phenylacetalddehyde citronellyl methyl acetal, phenylacetalddehyde diallylacetal, phenylacetalddehyde diamylacetal, phenylacetalddehyde dibenzylacetal, phenylacetalddehyde dibutyl acetal, phenylacetalddehyde diethylacetal, phenylacetalddehyde digeranylacetal, 20 phenylacetalddehyde dimethylacetal, phenylacetalddehyde ethyleneglycol acetal, phenylacetaldede glycerylacetal, citronellal cyclomonoglycolacetal, citronellal diethylacetal, citronellal dimethylacetal, citronellal diphenylethyl acetal, geranoxyacetalddehyde diethylacetal, and mixtures thereof.

“Ketal” refers to a ketal molecule wherein the carbonyl functional group of a 25 ketone is covalently bonded to two oxygen atoms of two hydroxyl groups at the same carbonyl carbon, namely, having a general structure  $CC(OC)_2C$ . Non-limiting examples of acetal perfume ingredients include acetone diethylketal, acetone dimethylketal, acetophenone diethyl ketal, methyl amyl catechol ketal, methyl butyl catechol ketal, and mixtures thereof.

30 Non-limiting examples of perfume ingredients being condensation products of amines and aldehydes, and not being preferred in the perfume compositions of the present

invention include anisaldehyde-methylanthranilate, aurantiol (hydroxycitronellal methylanthranilate), verdantiol (4-tert-butyl-alpha-methyldihydrocinnamaldehyde methyl anthranilate), vertosine (2,4-dimethyl-3-cyclohexene carbaldehyde), hydroxycitronellal ethylanthranilate, hydroxycitronellal linallylanthranilate, methyl-N-(4-(4-hydroxy-4-methylpentyl)-3-cyclohexenyl-methyldene)-anthranilate, methylnaphthylketone-methylanthranilate, methyl nonyl acetaldehyde methylanthranilate, methyl-N-(3,5,5-trimethylhexylidene) anthranilate, vanillin methylanthranilate, and mixtures thereof.

While not wishing to be bound by theory, it is believed that the porous mineral carriers of the present invention exert a catalytic effect that promotes the decomposition of these particular perfume ingredients.

The perfume compositions that are suitable for use in the present invention typically comprises less than about 30%, preferably less than about 15%, more preferably less than about 7%, even more preferably less than about 5%, yet even more preferably less than about 3%, and even more preferably less than about 1%, by weight of the perfume composition, of unstable perfume ingredients, preferably selected from the group consisting of allylic alcohol ester, secondary alcohol ester, tertiary alcohol ester, allylic ketone, condensation product of amines and aldehydes, and mixtures thereof, more preferably, allylic alcohol ester, secondary alcohol ester, tertiary alcohol ester, allylic ketone, acetal, ketal, condensation product of amines and aldehydes, and mixtures thereof.

A "stable" perfume ingredient can be loaded into activated/dehydrated zeolite 13X in the same manner without substantial degradation, with typically at least about 50%, preferably at least 65%, more preferably at least about 80%, and even more preferably at least about 95% of that ingredient not decomposed into other by-products. A perfume molecule is also considered as "stable" when it is isomerized in the zeolite loading process into another structure with the same molecular weight. Non-limiting examples of such stable perfume ingredients include alpha-pinene and beta-pinene.

Thus, the perfume compositions that are suitable for use in the present invention typically comprises at least about 70%, preferably at least about 85%, more preferably at least about 93%, even more preferably at least about 95%, yet even more preferably at

least about 97%, and even more preferably at least about 99%, by weight of the perfume composition, of stable perfume ingredients.

Porous mineral carriers provide an advantageous benefit in that they can retain perfume ingredients for a slow release, including non-substantive ingredients. Therefore, 5 preferably, perfume compositions that are incorporated into the porous mineral carrier, for use in the compositions and articles of the present invention comprise at least about 30%, preferably at least about 50%, more preferably at least about 65%, of non-substantive perfume ingredients which are characterized by having a boiling point equal to or lower than about 250°C and/or having a ClogP being equal or smaller than about 3.

10 Non-limiting examples of such non-substantive perfume ingredients include amyl acetate, amyl propionate, anethol, anisic aldehyde, anisole, benzaldehyde, benzyl acetate, benzyl acetone, benzyl alcohol, benzyl butyrate, benzyl formate, benzyl iso valerate, benzyl propionate, camphor gum, carvacrol, laevo-carveol, d-carvone, laevo-carvone, citral (neral), citronellol, citronellyl acetate, citronellyl isobutyrate, citronellyl nitrile, 15 citronellyl propionate, para-cresol, para-cresyl methyl ether, cyclohexyl ethyl acetate, cuminic alcohol, cuminic aldehyde, cyclal C (3,5-dimethyl-3-cyclohexene-1-carboxaldehyde), para-cymene, decyl aldehyde, dimethyl benzyl carbinol, dimethyl octanol, diphenyl oxide, dodecalactone, ethyl acetate, ethyl aceto acetate, ethyl amyl ketone, ethyl benzoate, ethyl butyrate, ethyl hexyl ketone, ethyl phenyl acetate, 20 eucalyptol, eugenol, fenchyl alcohol, geraniol, geranyl nitrile, hexenol, beta gamma hexenol, hexenyl acetate, cis-3-hexenyl acetate, hexenyl isobutyrate, cis-3-hexenyl tiglate, hexyl acetate, hexyl formate, hexyl neopentanoate, hexyl tiglate, hydratropic alcohol, hydroxycitronellal, indole, alpha-irone, isoamyl alcohol, isobutyl benzoate, isomenthone, isononyl acetate, isononyl alcohol, isobutyl quinoline, isomenthol, para- 25 isopropyl phenylacetaldehyde, isopulegol, isopulegyl acetate, isoquinoline, cis-jasmone, lauric aldehyde (dodecanal), ligustral (2,4-dimethyl-3-cyclohexene-1-carboxaldehyde), linalool, linalool oxide, menthone, methyl acetophenone, para-methyl acetophenone, methyl amyl ketone, methyl anthranilate, methyl benzoate, methyl benzyl acetate, methyl chavicol, methyl eugenol, methyl heptenone, methyl heptine carbonate, methyl heptyl ketone, methyl hexyl ketone, methyl nonyl acetaldehyde, methyl octyl acetaldehyde, methyl salicylate, myrcene, nerol, nerol, gamma-nonalactone, nonyl acetate, nonyl 30

aldehyde, allo-ocimene, octalactone, octyl alcohol (octanol-2), octyl aldehyde, (d-limonene), phenoxy ethanol, phenyl acetaldehyde, phenyl ethyl acetate, phenyl ethyl alcohol, phenyl ethyl dimethyl carbinol, propyl butyrate, rose oxide, 4-terpinenol, alpha-terpineol, terpinolene, tonalid (6-acetyl-1,1,3,4,4,6-hexamethyl tetrahydronaphthalene),  
5 undecenal, veratrol (ortho-dimethoxybenzene), coumarin, dihydroeuginol, dihydro isojasmonate, ethyl cinnamate, ethyl maltol, ethyl-2-methyl butyrate, ethyl salicylate, ethyl vanillin, eugenyl acetate, eugenyl formate, eugenyl methyl ether, fructone, geranyl oxyacetaldehyde, heliotropin, hinokitiol, hydroxycitronellol, indole, isoeugenol, isoeugenyl acetate, isomenthone, lyral, methyl cinnamate, methyl dihydrojasmonate,  
10 methyl isobut enyl tetrahydropyran, methyl beta naphthyl ketone, para-anisic aldehyde, para hydroxy phenyl butanone, para-methoxy acetophenone, para methyl acetophenone, phenoxyethyl propionate, phenylacetaldehyde diethyl ether, phenylethyl oxyacetaldehyde, vanillin, and mixtures thereof.

Nonlimiting examples of stable perfume ingredients that have a significantly low detection threshold, useful in the compositions of the present invention, are ambrox (1,5,5,9-tetramethyl-1,3-oxatricyclotridecane), anethole, bacdanol (2-ethyl-4-(2,2,3-trimethyl-3-cyclopenten-1-yl)-2-buten-1-ol), benzyl acetone, benzyl salicylate, butyl anthranilate, calone, cetalox (2-ethyl-4-(2,2,3-trimethyl-3-cyclopenten-1-yl)-2-buten-1-ol), cinnamic alcohol, coumarin, Cyclal C (3,5-dimethyl-3-cyclohexene-1-carboxaldehyde),  
20 cymal (2-methyl-3-(para iso propylphenyl)propionaldehyde), 4-decenal, dihydro isojasmonate, gamma-dodecalactone, ebanol, ethyl anthranilate, ethyl-2-methyl butyrate, ethyl vanillin, eugenol, florhydral (3-(3-isopropylphenyl)butanol), fructone (ethyl-2-methyl-1,3-dioxolane-2-acetate), heliotropin, herbavert (3,3,5-trimethylcyclohexyl-ethyl ether), cis-3-hexenyl salicylate, indole, iso cyclo citral, isoeugenol, alpha-isomethylionone, keone, linal (para-tertiary butyl alpha-methyl hydrocinnamic aldehyde), linalool, lyral (4-(4-hydroxy-4-methyl-pentyl)3-cyclohexene-1-carboxaldehyde), methyl heptine carbonate, methyl anthranilate, methyl dihydrojasmonate, methyl isobut enyl tetrahydropyran, methyl beta naphthyl ketone, methyl nonyl ketone, beta naphthol methyl ether, nerol, para-anisic aldehyde, para hydroxy phenyl butanone, phenyl acetaldehyde, gamma-undecalactone, undecylenic aldehyde, vanillin, and mixtures thereof. Some of the low odor detection perfume ingredients are also non-substantive perfume ingredients.

In a preferred embodiment of the present invention, the perfume composition to be incorporated in the porous carrier does not consist of 0.2% allyl amyl glycolate, 0.31% damascenone, 0.51% decyl aldehyde, 15.27% dihydro iso jasmonate, 1.02% helional, 14.97% ionone gamma methyl, 20.37% linalool, 1.02% myrcene, 15.27% p.t. bucinal, 5 0.51% para methyl acetophenone, 20.37% phenyl ethyl alcohol, and 10.18% undecavertol, by weight of the perfume composition. In another preferred embodiment, the perfume composition to be incorporated in the porous carrier does not consist of 10% benzyl salicylate, 5% coumarin, 2% ethyl vanillin, 10% ethylene brassylate, 15% galaxolide, 20% hexyl cinnamic aldehyde, 10% gamma methyl ionone, 15% lilial, 5% methyl dihydrojasmonate, 5% patchouli, and 3% tonalid. In yet another preferred embodiment, the perfume composition to be incorporated in the porous carrier preferably comprises less than about 100% aldehyde and/or acetal perfume ingredients. In addition, perfume composition to be incorporated in the porous carrier preferably comprises less than 45% terpinol, by weight of the perfume composition.

15        Optionally, free, stable and/or unstable perfume ingredients, including non-substantive perfume ingredients can be incorporated or encapsulated in other types of perfume carriers, for use in the compositions and articles of the present invention. Thus, the perfume can be encapsulated in the form of molecular encapsulation, such as inclusion in a complex with cyclodextrin, coacevate microencapsulation wherein the perfume 20 droplet is enclosed in a solid wall material, and "cellular matrix" encapsulation wherein solid particles contain perfume droplets stably held in cells or perfume is embedded in, e.g., starch or sugar matrix. These preferred optional perfume carriers, which can be useful in the present invention, are disclosed in PCT Publication WO 01/85888 published Nov. 15, 2001.

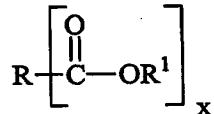
25        The perfume active may also include pro-fragrances such as acetal profragrances, ketal pro-fragrances, ester pro-fragrances (e.g., digeranyl succinate), hydrolyzable inorganic-organic pro-fragrances, and mixtures thereof. These pro-fragrances may release the perfume material as a result of simple hydrolysis, or may be pH-change-triggered pro-fragrances (e.g. pH drop) or may be enzymatically releasable pro-30 fragrances.

These pro-fragrances, pro-perfumes, pro-accords, and mixtures thereof hereinafter are known collectively as "pro-fragrances". The pro-fragrances of the present invention can exhibit varying release rates depending upon the pro-fragrance chosen. In addition, the pro-fragrances of the present invention can be admixed with the fragrance raw materials that are released therefrom to present the user with an initial fragrance, scent, accord, or bouquet.

The pro-fragrances of the present invention can be suitably admixed with any carrier provided the carrier does not catalyze or in other way promote the pre-mature release form the pro-fragrance of the fragrance raw materials. Preferably the pro-fragrances are not incorporated into the dehydrated/activated zeolite carriers.

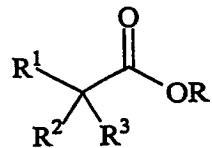
The following are non-limiting classes of pro-fragrances according to the present invention.

Esters and polyesters - The esters and polyester pro-fragrances of the present invention are capable of releasing one or more fragrance raw material alcohols. Preferred are esters having the formula:

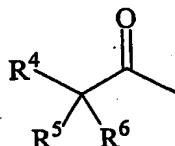


wherein R is substituted or unsubstituted C<sub>1</sub>-C<sub>30</sub> alkylene, C<sub>2</sub>-C<sub>30</sub> alkenylene, C<sub>6</sub>-C<sub>30</sub> arylene, and mixtures thereof; -OR<sup>1</sup> is derived from a fragrance raw material alcohol having the formula HOR<sup>1</sup>, or alternatively, in the case wherein the index x is greater than 1, R<sup>1</sup> is hydrogen thereby rendering at least one moiety a carboxylic acid, -CO<sub>2</sub>H unit, rather than an ester unit; the index x is 1 or greater. Non-limiting examples of preferred polyester pro-fragrances include digeranyl succinate, dicitronellyl succinate, digeranyl adipate, dicitronellyl adipate, and the like.

Beta-Ketoesters - The  $\beta$ -ketoesters of the present invention are capable of releasing one or more fragrance raw materials. Preferred  $\beta$ -ketoesters according to the present invention have the formula:



wherein -OR derives from a fragrance raw material alcohol; R<sup>1</sup>, R<sup>2</sup>, and R<sup>3</sup> are each independently hydrogen, C<sub>1</sub>-C<sub>30</sub> alkyl, C<sub>2</sub>-C<sub>30</sub> alkenyl, C<sub>1</sub>-C<sub>30</sub> cycloalkyl, C<sub>2</sub>-C<sub>30</sub> alkynyl, C<sub>6</sub>-C<sub>30</sub> aryl, C<sub>7</sub>-C<sub>30</sub> alkylenearyl, C<sub>3</sub>-C<sub>30</sub> alkyleneoxyalkyl, and mixtures thereof, provided at least one R<sup>1</sup>, R<sup>2</sup>, or R<sup>3</sup> is a unit having the formula:

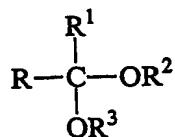


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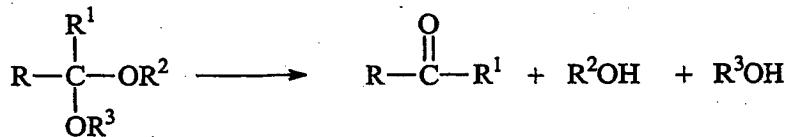
wherein R<sup>4</sup>, R<sup>5</sup>, and R<sup>6</sup> are each independently hydrogen, C<sub>1</sub>-C<sub>30</sub> alkyl, C<sub>2</sub>-C<sub>30</sub> alkenyl, C<sub>1</sub>-C<sub>30</sub> cycloalkyl, C<sub>1</sub>-C<sub>30</sub> alkoxy, C<sub>6</sub>-C<sub>30</sub> aryl, C<sub>7</sub>-C<sub>30</sub> alkylenearyl, C<sub>3</sub>-C<sub>30</sub> alkyleneoxyalkyl, and mixtures thereof, or R<sup>4</sup>, R<sup>5</sup>, and R<sup>6</sup> can be taken together to form a C<sub>3</sub>-C<sub>8</sub> aromatic or non-aromatic, heterocyclic or non-heterocyclic ring.

10 Non-limiting examples of b-ketoesters according to the present invention include 2,6-dimethyl-7-octen-2-yl 3-(4-methoxyphenyl)-3-oxo-propionate; 3,7-dimethyl-1,6-octadien-3-yl 3-(nonanyl)-3-oxo-propionate; 9-decen-1-yl 3-(b-naphthyl)-3-oxo-propionate; (a,a-4-trimethyl-3-cyclohexenyl)methyl 3-(b-naphthyl)-3-oxo-propionate; 3,7-dimethyl-1,6-octadien-3-yl 3-(4-methoxyphenyl)-3-oxo-propionate; 2,6-dimethyl-7-3,7-dimethyl-1,6-octadien-3-yl 3-(b-naphthyl)-3-oxo-propionate; 2,6-dimethyl-7-octen-2-yl 3-(4-nitrophenyl)-15 octen-2-yl 3-(b-naphthyl)-3-oxo-propionate; 2,6-dimethyl-7-octen-2-yl 3-(4-methoxyphenyl)-3-oxo-propionate; 3,7-dimethyl-1,6-octadien-3-yl 3-(a-naphthyl)-3-oxo-propionate; *cis* 3-hexen-1-yl 3-(b-naphthyl)-3-oxo-propionate; 2,6-dimethyl-7-octen-2-yl 3-(nonanyl)-3-oxo-propionate; 2,6-dimethyl-7-octen-2-yl 3-oxo-butyrate; 3,7-dimethyl-1,6-octadien-3-yl 3-oxo-butyrate; 20 2,6-dimethyl-7-octen-2-yl 3-(b-naphthyl)-3-oxo-2-methylpropionate; 3,7-dimethyl-1,6-octadien-3-yl 3-(b-naphthyl)-3-oxo-2,2-dimethylpropionate; 3,7-dimethyl-1,6-octadien-3-yl 3-(b-naphthyl)-3-oxo-2-methylpropionate; 3,7-dimethyl-2,6-octadienyl 3-(b-naphthyl)-3-oxo-propionate; 3,7-dimethyl-2,6-octadienyl 3-heptyl-3-oxo-propionate.

25 Acetals and Ketals - Another class of compound useful as pro-accords according to the present invention are acetals and ketals having the formula:



wherein hydrolysis of the acetal or ketal releases one equivalent of aldehyde or ketone and two equivalents of alcohol according to the following scheme:

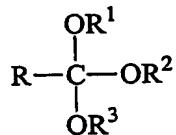


wherein R is C<sub>1</sub>-C<sub>20</sub> linear alkyl, C<sub>4</sub>-C<sub>20</sub> branched alkyl, C<sub>6</sub>-C<sub>20</sub> cyclic alkyl, C<sub>6</sub>-C<sub>20</sub> branched cyclic alkyl, C<sub>6</sub>-C<sub>20</sub> linear alkenyl, C<sub>6</sub>-C<sub>20</sub> branched alkenyl, C<sub>6</sub>-C<sub>20</sub> cyclic alkenyl, C<sub>6</sub>-C<sub>20</sub> branched cyclic alkenyl, C<sub>6</sub>-C<sub>20</sub> substituted or unsubstituted aryl, preferably the moieties which substitute the aryl units are alkyl moieties, and mixtures thereof. R<sup>1</sup> is hydrogen, R, or in the case wherein the pro-accord is a ketal, R and R<sup>1</sup> can be taken together to form a ring. R<sup>2</sup> and R<sup>3</sup> are independently selected from the group consisting of C<sub>5</sub>-C<sub>20</sub> linear, branched, or substituted alkyl; C<sub>4</sub>-C<sub>20</sub> linear, branched, or substituted alkenyl; C<sub>5</sub>-C<sub>20</sub> substituted or unsubstituted cyclic alkyl; C<sub>5</sub>-C<sub>20</sub> substituted or unsubstituted aryl, C<sub>2</sub>-C<sub>40</sub> substituted or unsubstituted alkyleneoxy; C<sub>3</sub>-C<sub>40</sub> substituted or unsubstituted alkyleneoxyalkyl; C<sub>6</sub>-C<sub>40</sub> substituted or unsubstituted alkylenearyl; C<sub>6</sub>-C<sub>32</sub> substituted or unsubstituted aryloxy; C<sub>6</sub>-C<sub>40</sub> substituted or unsubstituted alkyleneoxyaryl; C<sub>6</sub>-C<sub>40</sub> oxyalkylenearyl; and mixtures thereof.

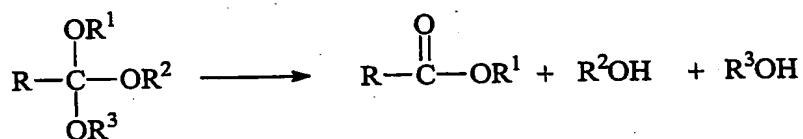
Non-limiting examples of aldehydes which are releasable by the acetals of the present invention include 4-(4-hydroxy-4-methylpentyl)-3-cyclohexene-1-carboxaldehyde (lyral), phenylacetaldehyde, methylnonyl acetaldehyde, 2-phenylpropan-1-al (hydrotropaldehyde), 3-phenylprop-2-en-1-al (cinnamaldehyde), 3-phenyl-2-pentylprop-2-en-1-al (a-amylcinnamaldehyde), 3-phenyl-2-hexylprop-2-enal (a-hexylcinnamaldehyde), 3-(4-isopropylphenyl)-2-methylpropan-1-al (cyclamen aldehyde), 3-(4-ethylphenyl)-2,2-dimethylpropan-1-al (floral ozone), 3-(4-*tert*-butylphenyl)-2-methylpropanal, 3-(3,4-methylenedioxyphenyl)-2-methylpropan-1-al (helional), 3-(4-ethylphenyl)-2,2-dimethylpropanal, 3-(3-isopropylphenyl)butan-1-al (florhydral), 2,6-dimethylhep-5-en-1-al (melonal), n-decanal, n-undecanal, n-dodecanal, 3,7-dimethyl-2,6-octadien-1-al (citral), 4-methoxybenzaldehyde (anisaldehyde), 3-methoxy-4-hydroxybenzaldehyde (vanillin), 3-ethoxy-4-hydroxybenzaldehyde (ethyl vanillin), 3,4-methylenedioxybenzaldehyde (heliotropin), 3,4-dimethoxybenzaldehyde.

Non-limiting examples of ketones which are releasable by the ketals of the present invention include a-damascone, b-damascone, d-damascone, b-damascenone, muscone, 6,7-dihydro-1,1,2,3,3-pentamethyl-4(5H)-indanone (cashmeran), *cis*-jasmone, dihydrojasmone, a-ionone, b-ionone, dihydro-b-ionone, g-methyl ionone, a-*iso*-methyl ionone, 4-(3,4-methylenedioxyphenyl)butan-2-one, 4-(4-hydroxyphenyl)butan-2-one, methyl b-naphthyl ketone, methyl cedryl ketone, 6-acetyl-1,1,2,4,4,7-hexamethyltetralin (tonalid), *l*-carvone, 5-cyclohexadecen-1-one, acetophenone, decatone, 2-[2-(4-methyl-3-cyclohexenyl-1-yl)propyl]cyclopentan-2-one, 2-*sec*-butylcyclohexanone, b-dihydro ionone, allyl ionone, a-irone, a-cetone, a-irisone, acetanisole, geranyl acetone, 1-(2-methyl-5-isopropyl-2-cyclohexenyl)-1-propanone, acetyl diisoamylene, methyl cyclocitronone, 4-*t*-pentyl cyclohexanone, p-*t*-butylcyclohexanone, o-*t*-butylcyclohexanone, ethyl amyl ketone, ethyl pentyl ketone, menthone, methyl-7,3-dihydro-2H-1,5-benzodioxepine-3-one, fenchone.

15 Orthoesters - Another class of compound useful as pro-accords according to the present invention are orthoesters having the formula:



wherein hydrolysis of the orthoester releases one equivalent of an ester and two equivalents of alcohol according to the following scheme:



20 wherein R is hydrogen, C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>4</sub>-C<sub>20</sub> cycloalkyl, C<sub>6</sub>-C<sub>20</sub> alkenyl, C<sub>6</sub>-C<sub>20</sub> aryl, and mixtures thereof; R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> are each independently selected from the group consisting of C<sub>5</sub>-C<sub>20</sub> linear, branched, or substituted alkyl; C<sub>4</sub>-C<sub>20</sub> linear, branched, or substituted alkenyl; C<sub>5</sub>-C<sub>20</sub> substituted or unsubstituted cyclic alkyl; C<sub>5</sub>-C<sub>20</sub> substituted or unsubstituted aryl, C<sub>2</sub>-C<sub>40</sub> substituted or unsubstituted alkyleneoxy; C<sub>3</sub>-C<sub>40</sub> substituted or unsubstituted alkyleneoxyalkyl; C<sub>6</sub>-C<sub>40</sub> substituted or unsubstituted alkylenearyl; C<sub>6</sub>-C<sub>32</sub> substituted or unsubstituted aryloxy; C<sub>6</sub>-C<sub>40</sub> substituted or unsubstituted alkyleneoxyaryl; C<sub>6</sub>-C<sub>40</sub> oxyalkylenearyl; and mixtures thereof.

Non-limiting examples of orthoester pro-fragrances include tris-geranyl orthoformate, tris(*cis*-3-hexen-1-yl) orthoformate, tris(phenylethyl) orthoformate, bis(citronellyl) ethyl orthoacetate, tris(citronellyl) orthoformate, tris(*cis*-6-nonenyl) orthoformate, tris(phenoxyethyl) orthoformate, tris(geranyl, neryl) orthoformate (70:30 geranyl:neryl), tris(9-decenyl) orthoformate, tris(3-methyl-5-phenylpentanyl) orthoformate, tris(6-methylheptan-2-yl) orthoformate, tris[4-(2,2,6-trimethyl-2-cyclohexen-1-yl)-3-buten-2-yl] orthoformate, tris[3-methyl-5-(2,2,3-trimethyl-3-cyclopenten-1-yl)-4-penten-2-yl] orthoformate, trismenthyl orthoformate, tris(4-isopropylcyclohexylethyl-2-yl) orthoformate, tris-(6,8-dimethylnonan-2-yl) orthoformate, tris-phenylethyl orthoacetate, tris(*cis*-3-hexen-1-yl) orthoacetate, tris(*cis*-6-nonenyl) orthoacetate, tris-citronellyl orthoacetate, bis(geranyl) benzyl orthoacetate, tris(geranyl) orthoacetate, tris(4-isopropylcyclohexylmethyl) orthoacetate, tris(benzyl) orthoacetate, tris(2,6-dimethyl-5-heptenyl) orthoacetate, bis(*cis*-3-hexen-1-yl) amyl orthoacetate, and neryl citronellyl ethyl orthobutyrate.

Pro-fragrances are suitably described in the following: U.S. 5,378,468 Suffis et al., issued January 3, 1995; U.S. 5,626,852 Suffis et al., issued May 6, 1997; U.S. 5,710,122 Sivik et al., issued January 20, 1998; U.S. 5,716,918 Sivik et al., issued February 10, 1998; U.S. 5,721,202 Waite et al., issued February 24, 1998; U.S. 5,744,435 Hartman et al., issued April 25, 1998; U.S. 5,756,827 Sivik, issued May 26, 1998; U.S. 5,830,835 Severns et al., issued November 3, 1998; U.S. 5,919,752 Morelli et al., issued July 6, 1999; WO 00/02986 published Jan. 20, 2000, Busch et al.; and WO 01/04248 published Jan. 18, 2001, Busch et al. all of which are incorporated herein by reference.

b) Optional Perfume Fixative

Optionally, the perfume active or mixture of actives may be combined with a perfume fixative. The perfume fixative materials employed herein are characterized by several criteria that make them especially suitable in the practice of this invention. Dispersible, toxicologically acceptable, non-skin irritating, inert to the perfume, degradable and/or available from renewable resources, and relatively odorless fixatives are used. The use of perfume fixatives is believed to slow the evaporation of more volatile components of the perfume.

Examples of suitable fixatives include members selected from the group consisting of diethyl phthalate, musks, and mixtures thereof. If used, the perfume fixative may comprise from about 10% to about 50%, and preferably from about 20% to about 40%, by weight of the perfume.

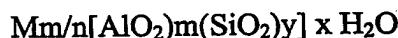
5        2.    Carrier materials

It is preferable that at least a major part of the perfume be contained or adsorbed to a carrier to prevent premature loss, as well as to avoid a strong product perfume odor. The encapsulation can be in the form of molecular encapsulation such as inclusion in a complex with cyclodextrin. Also, perfumes and other organic fabric care actives can be 10 absorbed onto the surface or adsorbed into the pores of porous carrier materials or embedded in a matrix, such as a starch or sugar matrix. As used herein, "porous carrier materials" includes porous solids selected from the group consisting of amorphous silicates, crystalline non-layer silicates, layered silicates, calcium carbonates, calcium/sodium carbonate double salts, sodium carbonates, clays, zeolites, sodalites, 15 alkali metal phosphates, macroporous zeolites, chitin microbeads, carboxyalkylcelluloses, carboxyalkylstarches, foams, porous starches, chemically modified starches, starch derivatives, low and high molecular weight sugars, and sugar derivatives, and mixtures thereof.

The selection of the most suitable method of perfume delivery takes into account 20 the effectiveness, the efficiency, and the cost of each method. Perfume loaded into Zeolite X or Y is preferred for its effectiveness, ease of processing, and low cost. The zeolite cavity protects and retains the perfume ingredients from physical effects in the absence of more than about 20% relative humidity (e.g., no rupture/perfume loss during processing, packaging, shipping, and storing of the product, or perfume loss from 25 diffusion) and from chemical effects (e.g., degradation during storage). The perfume composition is preferably released by a moisture activated mechanism wherein the perfume components are released upon being contacted with liquid or vapor water, preferably water vapor.

Preferred perfume carrier materials are zeolite X, zeolite Y and mixtures thereof. 30 The term zeolite as used herein refers to a crystalline aluminosilicate material. The

structural formula of a zeolite is based on the crystal unit cell, the smallest unit of structure represented by



where n is the valence of the cation M, x is the number of water molecules per unit cell, 5 m and y are the total number of tetrahedra per unit cell, and y/m is 1 to 100. Most preferably, y/m is 1 to 5. The cation M can be Group IA and Group IIA elements, such as sodium, potassium, magnesium and calcium. The aluminosilicate zeolite materials useful in the practice of this invention are commercially available. The preferred zeolite is a 10 faujasite-type zeolite including Type X Zeolite or Type Y Zeolite, both with nominal pore size of about 8 Angstrom units, typically in the range of 7.4 to 10 Angstrom units. Methods for producing X and Y-type zeolites are well known and available in standard texts.

For purposes of illustration and not by way of limitation, in a preferred embodiment, the crystalline aluminosilicate material is Type X and is selected from the 15 following:

- (I)  $Na_{86}[AlO_2]_{86}(SiO_2)_{106} \cdot xH_2O$ ,
- (II)  $K_{86}[AlO_2]_{86}(SiO_2)_{106} \cdot xH_2O$ ,
- (III)  $Ca_{40}Na_6[AlO_2]_{86}(SiO_2)_{106} \cdot xH_2O$ ,
- (IV)  $Sr_{21}Ba_{22}[AlO_2]_{86}(SiO_2)_{106} \cdot xH_2O$ ,

20 and mixtures thereof, wherein x is from about 0 to about 276. Zeolites of Formula I and II have a nominal pore size or opening of 8.4 Angstrom units. Zeolites of Formulas III and IV have a nominal pore size or opening of 8.0 Angstrom units.

In another preferred embodiment, the crystalline aluminosilicate materials is Type Y and is selected from the following:

25 (V)  $Na_{56}[AlO_2]_{56}(SiO_2)_{136} \cdot xH_2O$

(VI)  $K_{56}[AlO_2]_{56}(SiO_2)_{136} \cdot xH_2O$

and mixtures thereof, wherein x is from about 0 to about 276. Zeolites of Formulas V and VI have a nominal pore size or opening of 8.0 Angstrom units.

30 Zeolites used in the present invention are in particle form having an average particle size from about 0.1 microns to about 250 microns, preferably from about 0.1 microns to about 30 microns, and more preferably between about 1 micron and about 5

microns, as measured by standard particle size analysis techniques. Zeolites carrying perfume or other fabric care actives tend to agglomerate which facilitates the formation of an article and its dissolution when the active is displaced from the zeolite in solution. Different zeolites have a variety of different sizes and physical characteristics. A zeolite 5 or mixture of different zeolites are a preferred perfume carrier for use in the compositions and articles of the present invention.

Generally, zeolites useful in the compositions and articles of the present invention are described in U.S. Pat. No. 5,955,419 issued Sept. 21, 1999, to Barket, Jr., et al., which is incorporated herein by reference. However, different types of zeolites give different 10 performances as do zeolites that are of a common type but that have different physical properties. The following non-limiting examples of zeolites were evaluated for their dry fabric odor intensity, twenty four hours after the treatment of the fabrics: Zeolite 13X, MSHZ-128, MHSZ-Y and Y-Abscent, all commercially available from UOP; Advera 201N, commercially available from PQ Corporation; LSX, commercially available from 15 Zeoline; AX and X, commercially available from Vegobond; CVB 901, CVB 100, CVB 300, CVB 400, CVB 500, CVB 600, CVB 712, CVB 720, CVB 760 and CVB 780, all commercially available from Zeolist; AKZO-1 and AKZO-2, both commercially available from AKZO; and ENG-1, ENG-2, ENG-3, and ENG-4, all commercially available from Engelhard. The Zeolite 13X available from UOP exhibited the highest dry 20 fabric odor intensity, and thus is a preferred zeolite for use in the compositions and articles of the present invention.

Further, it has been found that different cations in the zeolite can also impact the dry fabric odor intensity. Specifically, zeolites having sodium cations are preferred over zeolites having potassium cations.

25 While a variety of zeolites having different properties are commercially available, zeolites may also be prepared using method well known in the art. Specifically, there are three primary methods for synthesis of zeolites, namely, (1) the hydrogel method which employs reactive oxides, soluble silicates, soluble aluminates, and caustic to produce high purity powders or zeolites in a gel matrix; (2) a clay conversion method which employs 30 raw minerals such as kaolin and faujisite, soluble silicates and caustic to produce low to high purity powder or zeolite in clay derived matrix; and (3) processes based on the use of

naturally occurring raw materials e.g. natural silica, acid treated clay, volcanic glass, amorphous minerals, to yield high purity powders and zeolites on ceramic supports. A preferred process for making a humidity triggered release zeolite, is the hydrogel method outlined above. A preferred type of zeolite for use in humidity-triggered release of 5 perfume is the X type zeolites, and more preferably, Zeolite 13X available from UOP.

The size of the zeolite particles allows them to be entrained in the fabrics with which they come in contact, however, there is a need to balance particle size with cleaning negatives. That is, large particles entrained in the fabric may be visible and generate the perception of ineffective cleaning, or impact the whiteness and/or color of 10 fabrics. Once established on the fabric surface, the zeolites can begin to release their incorporated perfume active(s), especially when subjected to humidity in the atmosphere.

### 3. Surface Area of Zeolite

Where the carrier material is a zeolite, it has been discovered that the selection of 15 zeolites that have the surface area characteristics described below provide improved perfume adsorption, deposition on fabrics and retention of the perfume composition through the laundering process to provide the treated fabrics with an enduring fragrance.

Types X and Y zeolites have a nominal pore sizes ranging from about 7.4 to about 10 Angstroms which is suitable for diffusion of perfume molecules into the zeolite cavity. Although pore size distribution and silicon to aluminum ratio (hydrophobicity of cavity), 20 cation, and moisture content are critical screening tools for selection among various types of zeolites such as zeolites A, X, Y, etc., there has previously been little guidance criteria for selecting a preferred zeolite from a given type of zeolites e.g. type X zeolites, for perfume delivery applications. Specifically, it has been found that there are significant differences amongst X-type zeolites, perhaps due to differences in synthesis.

An evaluation of type-X zeolites from UOP, L.L.C. (Zeolite 13X powder) and PQ 25 Corporation (Advera 201N powder) confirmed that although Zeolite 13X and Advera 201N have an identical chemical composition, particle size distribution, cation, pH (1wt% aqueous dispersion), and provide equivalent deposition onto fabric, there is a significant difference in BET surface area between these two type X zeolites. BET surface area is an 30 estimate of the total adsorption area of a nitrogen monolayer adsorption in a porous particle. The procedure, well known to those familiar in the art, and consists of several

steps including (1) placing the porous particles in a glass tube, approximately  $\frac{1}{2}$  full, (2) applying a high vacuum to remove adsorbed species, (3) cooling of the powder sample to approximately 76 Kelvin, (4) evaluating the adsorptive capacity of the powder as a function of the partial pressure of nitrogen injected into the tube. The adsorption data is 5 then organized to yield a total surface area for nitrogen adsorption (monolayer). In order to avoid erroneous results, a change in the standard protocol for BET surface area measurement is recommended, namely, do not purge the powder sample with liquid nitrogen for about 24 hours prior to analysis as the zeolite may begin to adsorb water vapor from ambient conditions during the purge operation, resulting in a high standard 10 deviation in the BET surface area results (about  $33 \text{ m}^2/\text{g}$  compared to about  $3 \text{ m}^2/\text{g}$ ).

The BET surface area data for Zeolite 13X and Advera 201N are tabulated below. Advera 201N and Zeolite 13X (both type X zeolites) had an average BET surface area of about  $587 \text{ m}^2/\text{g}$  and about  $478 \text{ m}^2/\text{g}$  respectively.

Table A

## 15 Gemini BET surface area measurement for UOP Zeolite 13X

Total Moisture Content (wt%)	Nitrogen Purge Time (hrs)	Zeolite Source	BET Surface Area ( $\text{m}^2/\text{g}$ )
6.8%	0	13X from UOP	587
6.8%	0	13X from UOP	585
6.8%	0	13X from UOP	588
6.8%	0	13X from UOP	589
6.8%	0	13X from UOP	588
6.8%	0	13X from UOP	586
6.8%	0	13X from UOP	589
12.8%	0	13X from UOP	359
20.7%	0	13X from UOP	13
6.8%	3.75	13X from UOP	507
6.8%	8.0	13X from UOP	555
6.8%	23.0	13X from UOP	559

6.8%	24	13X fromUOP	576
6.8%	24	13X fromUOP	594
8.0%	0	Advera 201N – PQ	477
8.0%	0	Advera 201N - PQ	479
8.0%	0	Advera 201N-PQ	473
8.0%	0	Advera 201N-PQ	482
8.0%	0	Advera 201N-PQ	476
8.0%	0	Advera 201N-PQ	478

5 Although PQ Corporation's Advera 201N, an X type zeolite had a higher overall perfume retention efficiency, it is believed that it would hold onto perfume components too tightly resulting in a odor release profile that would be too slow for a consumer laundry product. Of course, it is anticipated that there will be other perfume release applications that require a slower more controlled release. The deposition of UOP Zeolite 13X onto fabrics via a laundering process provides the preferred odor release profile that improves perfume character and intensity on dried fabrics.

10 Preferred type X zeolites will have a total moisture content that is less than about 7wt%, and a BET surface area that is at least about 475 m<sup>2</sup>/g, preferably greater than about 525 m<sup>2</sup>/g, and more preferably greater than about 580 m<sup>2</sup>/g.

#### 4. Perfume Entrapment in Zeolite

15 The zeolites to be used herein preferably contain less than about 10% desorbable water, more preferably less than about 8% desorbable water and even more preferably less than about 5% desorbable water. Such materials may be obtained by first activating/dehydrating by heating the zeolite from about 150° to about 350°C, optionally at a reduced pressure from about 0.001 to about 20 Torr, for at least about 12 hours. After this "activation", the perfume active or perfume composition is thoroughly mixed with the activated zeolite and, optionally, heated to about 60°C for up to two hours to 20 accelerate absorption equilibrium within the zeolite particles. The perfume zeolite

mixture is then cooled to room temperature, under controlled humidity conditions, at which time the mixture is in the form of a free flowing powder.

The amount of perfume incorporated into the zeolite carrier is less than about 20%, typically less than about 18.5% and more typically less than about 17%, and even 5 more typically from about 12% to about 15% by weight of the loaded particles, given the limits on the pore volume of the zeolite. Excess perfume materials and non-deliverable perfume materials that are not incorporated into zeolite pores are likely to be immediately released to the wash or rinse solution upon contact with the aqueous medium. In the case of perfume articles, an optional excess of "free" perfume will provide a desirable 10 immediate "bloom" of the fragrance upon dispensing the article in a laundry solution.

The mixing and entrapment of perfume active into the perfume carrier can be carried out using various techniques known in the art of adsorption, absorption, and agglomeration. The perfume active (100% active or diluted in a solvent) can be sprayed onto a bed of powder, followed by mixing. Alternatively, the perfume can be loaded in 15 the vapor or superheated phase. Another option is to use a rotating drum mixer, and spray-on perfume active via single fluid, two-fluid, ultrasonic, or other nozzle technology. One can also use continuous agglomerating equipment, well-known to those familiar in the art, to entrap perfume in the perfume carrier. Most often, perfume actives are adsorbed or absorbed onto perfume carriers by simply mixing the perfume active with the 20 carrier in a bulk mixer, typically a rotating drum mixer. There are however several limitations when using such equipment for perfume entrapment in zeolite, namely (1) the difficulty of controlling the contact between the perfume active and carrier, (2) the limited ability to control heat transfer, (3) the fracture of perfume carrier particles under intense agitation, (4) inability to operate on a continuous basis, and (5) large space requirement 25 for equipment.

Not to be limited by theory, but it is believed that perfume entrapment in zeolite involves key physical and chemical transformations including: (1) perfume adsorption onto zeolite surface, (2) perfume diffusion into the zeolite cavities, (3) the "binding" of perfume active to a site in the zeolite cavity, (4) intermolecular interactions which lead to 30 selective entrapment of materials in a specific order, (5) the distortion of aluminosilicate

lattice of the zeolite cavity; and (6) the binding of perfume molecules to various sites, near the surface as well as within the diffusion pores.

Adsorption of perfume molecules into zeolite is governed by two stages, specifically, (1) the energetics during initial entrapment, and (2) entropy management at 5 higher levels of perfume inside the cavity. That is, at low loadings, the perfume molecule that "fits" better into the pore space is able to offer the best energy state, favoring its adsorption. At higher levels of perfume loading, there is increased demand to pack as many molecules as possible in the zeolite cavity and smaller molecules begin to dominate the pore space. This model has been verified by the behavior of several systems, 10 including Xenon/Argon, Xenon/Methane, and Carbon Dioxide/Dichlorofluoromethane.

Moreover, perfume adsorption into the zeolite cavity results in a large exothermic release of energy. Typically, the temperature rise of the bulk powder is about 20° to about 40°C. In turn, the increase in particle temperature influences the selectivity of 15 perfume molecules adsorbed (energy released meets the activation energy requirements for adsorption of specific molecules). By controlling the heat transfer during the perfume adsorption operation it is possible to manipulate (1) the quantity of perfume adsorbed, (2) the selectivity of perfume molecules adsorbed into the cavity, and (3) the retention of the adsorbed perfume molecules through a laundering process.

In order to accomplish the objective of higher quantity of perfume active 20 entrapped inside the zeolite cavity, and higher retention of adsorbed perfume active through a laundering step, it is desired to allow the perfume carrier to reach its maximum temperature prior to cooling of the zeolite particle. Once the maximum temperature is reached, loading governed by energetics is nearly complete. To facilitate the inclusion of the smaller molecules in the zeolite cavity, and to minimize evaporative loss of perfume 25 components, the zeolite particle should be cooled.

Since the kinetics of adsorption of each perfume active will be different, one needs to first run a "blank" (no heat removal) to prepare a temperature-time profile. From 30 this temperature-time profile, estimate the time at which there is a change in slope (i.e. particle temperature begins to plateau). This is the time at which the particle must be cooled in order to minimize evaporative losses, and maximize adsorption of perfume components into the zeolite cavity. The amount of heat removed influences the final

temperature of the zeolite particle. Since each perfume active will have a different composition of volatile components, the influence of the final temperature on perfume retention will depend on the perfume composition.

By controlling the heat transfer in this manner, a higher quantity of perfume active can be entrapped in the zeolite cavity, and perhaps more importantly, a higher quantity of perfume active is retained within the zeolite cavity through the laundering process. That is, removal of heat at the right stage of perfume entrapment results in more effective perfume entrapment, and better protection of the perfume active through the washing/rinsing process during laundering.

By way of example, when perfume active is sprayed onto a bed of zeolite X that is agitated in a drum mixer, the heat transfer mechanism occurs through conduction and free convection. Conductive heat transfer is more effective than free convection. The sheet of powder on which perfume active has been sprayed back-mixes with cooler powder such that there is an immediate transfer of heat via conduction. The result is a small temperature rise, typically about 10°C to about 20°C upon targeting an approximate 15% by weight loading of perfume active in zeolite 13X.

In the alternative, a continuous mixer may be used wherein the perfume active and zeolite are contacted in a small volume zone with a very low residence time on the order of 1 to about 10 seconds in that contact zone. In this scenario, the modes of heat transfer again are conduction and convection. However, both modes of heat transfer are inefficient, since all of the powder in the small volume zone will reach a target temperature at generally the same time, such that there is no longer a large temperature gradient to promote conductive heat transfer. The result is a much higher temperature rise for the powder, typically on the order of about 30°C to about 60°C. This large increase in temperature promotes entrapment of perfume actives that have an activation energy barrier. When heat is removed from the zeolite after a maximum temperature has been reached, the retention of perfume materials inside the zeolite cavity is greatly improved.

The final temperature of the powder appears to be more critical than the medium used for cooling. Media evaluated for cooling are liquid nitrogen, powders that are inert to fragrance adsorption such as sodium citrate, sodium carbonate, citric acid etc., shell-

and-tube, and plate heat exchangers. The optimum final temperature of the powder will depend on the specific perfume active used and the effectiveness of liquid/solid contacting in the mixer.

A preferred process for entrapping the perfume active in the perfume carrier 5 employs a continuous mixer that maximizes contact area between the perfume active and the perfume carrier. Ideally, the mean droplet diameter of the atomized perfume active is close to or smaller than the mean particle size of the perfume carrier. In the preferred embodiment of the invention, the size of the perfume carrier is less than about 100 microns, preferably less than about 40, more preferably less than about 30 microns, and 10 even more preferably less than about 5 microns. Also, the heat removal from the perfume carrier commences once the particle has reached a maximum temperature.

Perfume entrapment in zeolite powder results in a significant increase in dry fabric odor intensity, both initially and after several weeks of fabric storage. The increase in enduring fabric odor intensity is particularly significant relative to perfume actives that 15 are dispensed directly to laundry solutions without zeolite. Example 3 serves to demonstrate that the zeolite and perfume technology disclosed herein delivers significant improvements in dry fabric odor intensity, both initially and after at least about 2 weeks of fabric ageing. Examples 4-6 exemplify various means for achieving higher entrapment and retention of perfume with zeolite.

20

### EXAMPLE 3

#### *Perfume with Zeolite vs. Perfume oil*

Control fabric samples were laundered in Tide® unscented granular laundry detergent with a perfume composition which was added directly to the wash cycle solution. A second set of fabrics were laundered in the same detergent with the same 25 perfume at the same levels, but with the perfume being adsorbed onto Zeolite 13X before it being added to the wash cycle solution. The fabric samples were then rinsed and dried in a conventional dryer. The fabrics were then odor evaluated for odor intensity at the completion of the drying cycle. The fabrics were placed in loosely sealed aluminum foil bags for subsequent re-evaluation at seven and fourteen days after laundering. Odor 30 evaluation revealed that the perfume with zeolite provided a more intense dry fabric odor at each evaluation point vs the odor intensity provided by the perfume without zeolite,

and that the perfume with zeolite also maintained a relatively constant or enduring odor intensity over the test period.

EXAMPLE 4

*Combining Perfume with Zeolite Particles – Bench Scale* An amount of about 15g of perfume is slowly added (approx 0.08 g/sec) to about 85g of Zeolite X under high agitation in a conventional kitchen blender. A substantial temperature increase is recorded (about 20°C) apparently caused by intensive mixing and heat of adsorption of fragrance materials into the zeolite cage structure. The mixture is allowed to mix until the bulk temperature is about 25°C. A product yield of about 100g is analyzed by Gas Chromatography (after acetone treatment for about 1 hr at about 60°C, and extraction by hexane) with an assay of about 12wt% total fragrance in zeolite.

EXAMPLE 5

*Combining Perfume with Zeolite Particles – Plow Mixer*

An amount of about 150g of perfume is added at about 5 g/sec through a pressure nozzle (about 80 psi, droplet size of about 90 micrometers) to about 850g of Zeolite X under high agitation in a single batch Loedige plow mixer (nominally 200 RPM plow, 2000 RPM chopper, and 300 second cycle time). A cooling jacket at 20°C is used to remove the heat generated during fragrance entrapment (approx. 280 kJ/kg perfume). About 1000g of highly flowable powder is collected and analyzed by Gas Chromatography to yield about 15wt% total fragrance in zeolite. An after simulated wash treatment of zeolite (anionic surfactant wash) and analysis by Gas Chromatography gives a result of about 12wt% fragrance remaining inside the zeolite cage.

EXAMPLE 6

*Combining Perfume with Zeolite Particles – Schugi Mixer*

Perfume is added continuously at a rate of about 1.08 g/sec through a two-fluid nozzle (about 30 psi, mean droplet size of about 5 micrometers) simultaneously with about 6.12 g/sec of Zeolite 13X added via a screw feeder. The liquid fragrance and zeolite powder are contacted in a mixing zone consisting of a shaft with 3 blade components (each component fabricated with 6 blades for intense mixing), and a shaft rotation speed of about 2700-3500 RPM. The residence time of the powder in the

“agglomeration” zone is less than about 3 seconds. Substantial heating of the powder is detected within the 3 second residence time, from about 25° to about 80°C. The product is cooled using liquid nitrogen injection to achieve evaporative cooling. Sufficient liquid nitrogen is injected to obtain a product temperature of about 8°C. Gas Chromatography analysis results in about 15.5wt% total fragrance oil, and about 14.2wt% fragrance oil inside the zeolite cavity (after simulated anionic wash).

5 A tabulation of the various mixers and their effectiveness in entrapping and retaining perfume components inside Zeolite 13X is presented in Table B.

**Table B**

Sample Description	Total Oil in Zeolite (wt%)	After Simulated Wash-Oil in Zeolite (wt%)
PLZ from plow type batch mixer (heat removed using cooling water jacket, and powder acts as a heat sink)	16.7%	10.20%
No Heat Removal after zeolite/perfume contacting in Schugi FX100 continuous mixer	15.3%	11.30%
Sporadic Addition of Liquid N2 for heat removal after zeolite/perfume contacting in Schugi FX100 continuous mixer	15.2%	11.30%
Continuous addition of Liquid N2 after zeolite/perfume contacting in Schugi FX100 continuous mixer  (Maximum powder temperature 35°C)	15.4%	13.40%
Continuous addition of Liquid N2 after	15.5%	14.20%

zeolite/perfume contacting in Schugi FX continuous mixer (Maximum powder temperature 8°C)		
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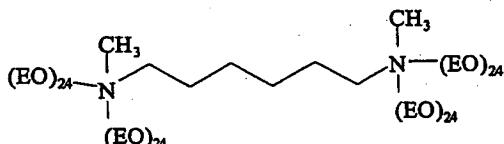
### C. Optionals

#### 1. Binder Material

The selection of a binder material, or agglomerating agent, for tablet making is preferred to ensure the ability to form a tablet and the stability of the tablet. Any binder material known in the art can be used. For example, materials that have a softening temperature above about 35°C, but preferably below about 200°C and more preferably below about 100°C are highly suitable. The softening point is defined as the glass transition temperature, if one exists, or the melting temperature. In general, suitable binders for use herein are those known to those skilled in the art and include anionic surfactants like C6-C20 alkyl or alkylaryl sulphonates or sulphates, preferably C8-C20 alkylbenzene sulphonates, fatty acids, fatty alcohols, cellulose derivatives such as carboxymethylcellulose and homo- or co- polymeric polycarboxylic acid or their salts, nonionic surfactants, preferably C10-C20 alcohol ethoxylates containing from 5-100 moles of ethylene oxide per mole of alcohol and more preferably the C15-C20 primary alcohol ethoxylates containing from 20-100 moles of ethylene oxide per mole of alcohol. Of these tallow alcohol ethoxylated with 25 moles of ethylene oxide per mole of alcohol (TAE25) or 50 moles of ethylene oxide per mole of alcohol (TAE50) are preferred. Other preferred binders include the polymeric materials like polyvinylpyrrolidones with an average molecular weight of from 12,000 to 700,000 and polyethylene glycols with an average molecular weight of from 600 to 10,000. Copolymers of maleic anhydride with ethylene, methylvinyl ether, methacrylic acid or acrylic acid are other examples of polymeric binders. Others binders further include C10-C20 mono and diglycerol ethers as well as C10-C20 fatty acids.

Binders that are especially useful in perfume articles containing a moisture-triggered perfume release are those materials that have a water content of less than about 10% by weight, preferably less than about 7% by weight, and more preferably less than

about 5% by weight of the article. Examples of such binders are polyethylene glycols with a softening temperature in the range of 35°C to 65°C. One can also use water-soluble polymers, such as polyethyleneamines, polyethoxylated amines or imines, which have a softening temperature in the range of 35° to 65°C. A preferred polyethylene ethoxylated amine structure is shown below;



#### Binder Screening Test

The following binder screening test has been developed for use in identifying other binder materials that are suitable for use in a perfume delivery composition/article composed of a hydrating material and/or moisture-triggered perfume carrier. The binder screening test comprises of several steps: (1) adding about 10g of perfume to about 90g of binder material in a fluid state; (2) thoroughly mix the perfume and binder; (3) allow the mixture sit overnight at ambient temperature; (4) determine the mass of free perfume in the mixture; and (5) calculate the bound perfume/binder content. The mass of free perfume may be determined by collecting liquid perfume from the surface of solid binder, using wet chemistry to separate the two distinct phases, or conducting a more complicated solvent extraction procedure.

A given binder material is appropriate for use in the compositions and articles of the present invention if the bound perfume content is less than about 5% by weight, and is preferably less than about 3% by weight of the binder material plus perfume mixture. Binder materials that are subjected to the described screening test and retain less than about 5% by weight perfume in the binder plus perfume mixture will not adversely affect the long-term temperature stability of the perfume article. For a perfume article composed of a hydrating material and a moisture sensitive perfume carrier, the ideal binder material will also have increased ionic character, decreased ethoxylation as ethoxylation tends to dissolve perfume molecules with similar moieties, and high water solubility such that it will be sparingly soluble in perfume materials.

Further, preferred binder materials will have rheological properties such that the material will become more fluid during the compression of tablet making. During

compression, the temperature of the composition will increase causing the binder to exceed its softening temperature. In this state, preferred binders will be more fluid and will have increased interaction with the other composition components. Further, this change in rheology helps to agglomerate fine particulates with coarser materials to bind them into a tablet form. The characteristics of the composition particles are critical during compression. Since the percentage of binder by weight is a strong function of the particle size of the composition, the composition components should be screened to an appropriate particle size distribution before tablet making. The optimum particle size for tablet making will depend on (a) the nature of the binder, where the binder's rheological properties are a function of temperature and the interaction of the binder with the other composition components, and (b) the percentage by weight of the binder per particle size fraction.

If the binder level is too high, the tablet formed will have high strength but long dissolution times. If the binder level is too low, the tablet will dissolve rapidly but its strength may be so poor that it is friable. Hence, the softening temperature of the binder is important to achieve good tablet strength and acceptable dissolution time while the chemical nature of the binder is important to minimize deactivation of the hydrating material and the perfume carrier during making and in-trade handling.

Binder selection is especially important in the case of compositions and articles that contain a perfume loaded zeolite. For example, hydrophilic binders tend to draw water into compositions/articles containing them and this moisture may adversely affect perfume retention inside the zeolite. Similarly, binder materials that have a low softening temperature may tend to extract perfume materials from within the zeolite cage, or alternatively, displace perfume materials from the cage structure. In addition, binder materials with a high softening temperature may lead to poor or prolonged dissolution times.

#### EXAMPLE 7

##### *Polyethylene Glycol as Binder*

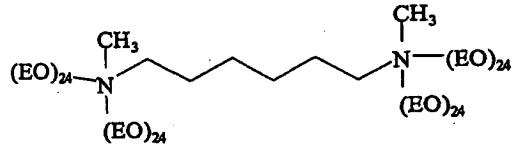
Polyethylene Glycol 1500 is a nonionic binder that melts between 45-55°C. About 30g of perfume loaded with zeolite is mixed with about 57g of citric acid/sodium carbonate granules that are prepared by compacting about 31.4g coarse citric acid and

about 25.7g fine sodium carbonate at about 100 kN compaction force. About 13g of Polyethylene Glycol 1500 at about 60°C is added to the mixture, under high agitation in a conventional kitchen mixer. The agglomerated powder is tableted using an Instron (at nominal 60 mm/min compression rate, 10 kN compaction force, and 18 mm diameter spherical tablet). The tablets are placed in sealed glass jars. Control tablets are stored at about 10°C and are used as a reference for tablets that are stored at about 50°C. The tablets are tested over two weeks to characterize the effect of the PEG. Tablets are used in the laundering of fabrics by adding the tablets to the wash cycle. During odor evaluation of fabrics treated with the tablets, it is determined that tablets that have been stored for about seven days at about 50°C give a significantly poorer dry fabric odor intensity performance relative to the control and tablets stored for about fourteen days at about 50°C give even poorer dry fabric odor intensity performance. Not to be bound by theory, but it is believed that the exposure of the tablets to high temperatures results in an increased mobility of PEG, which extracts perfume components from the zeolite leading to the loss in dry fabric odor intensity performance. Thus, PEG as a binder is acceptable if high temperature storage is not anticipated.

#### EXAMPLE 8

##### *Effect of Binder Selection*

The following example shows the effect of binder selection when higher temperature stability is important. Tablets (each spherical and composed of about 1.41g citric acid and about 1.15g sodium carbonate compacted particles, about 0.20g perfume in about 1.15g Zeolite 13X, and about 0.59g of a binder selected from (a) PEG 1500, (b) glycerol/sorbitol having a weight ratio of glycerol to sorbitol of about 70:30 and (c) a polyethylene ethoxylated amine having the structure:



25

The tablets are prepared as described in Example 2 and stored in sealed glass jars at about 5°C (about 1 wk), at about 38°C (about 2 wks) and at about 50°C (about 1 wk). After storage for the period indicated, the tablets are added to the rinse cycle of the laundry process, and the treated fabrics are dried and evaluated for their initial dry fabric odor

intensity. Specifically, it is found that the use of PEG 1500 reduces the initial dry fabric odor performance when the tablets are exposed to periods of high temperature. However, the glycerol/sorbitol and polyethylene ethoxylated amine binders give only very slightly diminished dry fabric odor intensity performance due to high temperature stress.

5 Therefore, these materials that pass the binder screening test criteria maintain the dry fabric odor intensity performance of the tablet even after stressed with high temperature testing.

## 2. Disintegrants

The articles of the present invention can also comprise one or more disintegrants 10 to provide improved or controlled dissolution. Suitable additional disintegrants include:

- a) non-cross linked polymeric disintegrants;
- b) water-soluble hydrated salts having a solubility in distilled water of at least about 25g/100g at 25°C; and
- c) mixtures thereof.

15 Preferred non-crosslinked polymeric disintegrants have a particle size distribution such that at least 90 % by weight of the disintegrant has a particle size below about 0.3mm and at least 30 % by weight thereof has a particle size below about 0.2mm. Suitably, the non-crosslinked polymeric disintegrant is selected from starch, cellulose and derivatives thereof, alginates, sugars, polyvinylpyrrolidones, swellable clays and mixtures 20 thereof.

The water-soluble hydrated salt, on the other hand, is preferably soluble to the extent of at least about 40g/100g, more preferably at least about 60g/100g of distilled water at about 25°C. In addition, the water-soluble hydrated salt preferably has a melting point in the range from about 30°C to about 95°C, more preferably from about 30°C to 25 about 75°C. Preferred water-soluble hydrated salts are selected from hydrates of sodium acetate, sodium metaborate, sodium orthophosphate, sodium dihydrogenphosphate, disodium hydrogen phosphate, sodium potassium tartrate, potassium aluminium sulphate, calcium bromide, calcium nitrate, sodium citrate, potassium citrate and mixtures thereof. Particularly suitable materials include sodium acetate trihydrate, sodium metaborate tetrahydrate or octahydrate, sodium orthophosphate dodecahydrate, sodium dihydrogen phosphate dihydrate, the di-, hepta- or dodeca-hydrate of disodium hydrogen phosphate, 30

sodium potassium tartrate tetrahydrate, potassium aluminium sulphate dodecahydrate, calcium bromide hexahydrate, tripotassium citrate monohydrate, calcium nitrate tetrahydrate and sodium citrate dihydrate. In preferred embodiments, the water-soluble hydrated salt is selected from water-soluble mono-, di- tri- and tetrahydrate salts and 5 mixtures thereof. Highly preferred herein is sodium acetate trihydrate, tripotassium citrate monohydrate, mixed alkali-metal citrates containing at least one potassium ion and mixtures thereof. Highly preferred are sodium acetate trihydrate and tripotassium citrate monohydrate.

### 3. Other Optional Materials

10 The compositions and articles of the present invention may further comprise one or more optional materials, including but not limited to, water soluble builders, surfactants, enzymes, organic polymer compounds having dispersant, anti-redeposition and/or soil releasing properties, metal ion sequestrants, crystal growth inhibitors, colorants, silicates, corrosion inhibitors, suds suppressing materials and other adjunct 15 materials that can function as solubility-triggers (e.g. responsive to pH, ion concentration or temperature), moisture sinks (for example hydratable but anhydrous or partially hydrated salts), and mixtures thereof.

In addition, the perfume delivery compositions of the present invention may also 20 include one or more fabric care actives selected from the group consisting of bodying agents, drape and form control agents, smoothness agents, static control agents, wrinkle control agents, sanitization agents, drying agents, stain resistance agents, soil release agents, malodor control agents, dye fixatives, dye transfer inhibitors, color maintenance agents, anti-fading agents, whiteness enhancers, anti-abrasion agents, fabric integrity agents, anti-wear agents, defoamers and anti-foaming agents, rinse aids, UV protection 25 agents, sun fade inhibitors, insect repellents, enzymes, and mixtures thereof. A description of these agents and their preparation may be obtained by reference to U.S.S.N. 09/838,863 filed April 20, 2001 by Caswell et al. which is incorporated herein by reference.

## 30 II. Articles Of The Present Invention

The articles of the present invention include a variety of application forms for the compositions described hereinabove, in combination with means for maintaining the stability of the compositions. In terms of application forms, the compositions are preferably particulate compositions that may be added directly to a laundry solution, 5 compositions formed into articles having a variety of shapes and sizes for dispensing in aqueous solutions, compositions adhered to substrates for use in dryer applications and in drawers and closets where fabrics are stored, and compositions placed in a gas permeable containers for use as room deodorizers and refreshers amongst other common perfume applications.

10 Stability in the context of the present compositions refers not only to the retention of the perfume in the zeolite pores but also to the stability of the other composition components and their ability to provide for the rapid dissolution of a composition or article in an aqueous solution. The stability is provided to the present compositions and articles by a variety of features of the compositions/articles themselves as well as the 15 packaging materials in which they are stored.

#### **A. Perfume and Zeolite or Hydrating Material**

The articles of the present invention will preferably comprise a perfume delivery composition as described hereinabove. However, the articles of the present invention may more simply comprise a perfume composition entrapped in zeolite or a perfume 20 composition combined with a hydrating material. To prevent the premature release of perfume components from such perfume delivery compositions, the composition components must be protected from atmospheric moisture or humidity during their processing, preparation, transport and storage. Packaging materials and characteristics required of such materials to sufficiently protect the perfume delivery compositions from 25 atmospheric moisture are described hereinafter.

There are also a number of additional preferred features of the perfume delivery compositions and articles formed from those compositions that contribute to the ability of the perfume article to retain perfume and rapidly dissolve when dispensed in an aqueous solution. Specifically, these features include (1) using fine powder materials that are compressed to restrict the diffusion of water into, and perfume out of, the perfume article; 30 (2) increasing the size of articles made from these perfume delivery compositions to

provide a lower total surface area for water adsorption relative to total surface area of the particulates in the compositions; (3) using a hot melt binder that will bind with water before it reaches the perfume carrier, and/or a binder that will not extract perfume actives from the perfume carrier; and (4) using the appropriate size article, particularly when 5 dispensing it into the rinse cycle of a washing machine using an automated dispenser. Also important is the ability to manufacture, package, and sell a unit dose perfume delivery article as a single use item or in a multi-pack without compromising product form or stability.

The size of the perfume delivery article may be limited by the method used to 10 dispense the article in the laundry solution. Where the article is dispensed directly into the solution the article can be any size that will be received in the machine tub. When a washing machine dispensing device is used, it is preferred that the article have a diameter or width between about 1mm and about 9mm and more preferably between about 5mm and about 8mm. When a self-contained dispensing device such as a Downy Ball® or 15 similar automatic dispensing device is used, it is preferred that the diameter or width be between about 1mm and about 30mm, more preferably between about 5mm and about 26mm, and even more preferably between about 8mm and 18mm so that the article easily passes through the opening of the dispensing device. When a European style washing machine is used, the perfume delivery article may be added to the fabric softener drawer, 20 however, in such a procedure it is preferred that the article have a diameter of less than about 18mm. A higher deposition of the perfume particles is observed and the initial dry fabric odor intensity is higher when the perfume compositions/articles are added to the rinse cycle versus the wash cycle.

#### EXAMPLE 9

##### *Tablets vs Free Perfume Oil*

About 30g of perfume loaded zeolite is mixed with about 57g of a citric acid/sodium carbonate coparticle (made by compacting about 31.4g coarse citric acid and about 25.7g fine sodium carbonate at about 100 kN compaction force). Approximately 30 13g of Polyethylene Glycol 1500 at about 50°C, is added to the mixture, under high agitation in a conventional kitchen mixer. The agglomerated powder is tableted using an Instron (at nominal 60 mm/min compression rate, 10 kN compaction force, and 18 mm

diameter spherical tablet). Two tablets are placed in a washing machine during the wash cycle. No cleaning disbenefits are noted (whiteness maintenance of fabrics is not impacted, no impact on soil removal from fabrics, nil residue inside the washer, no undesirable impact on colored or white clothes of different fabric types). In a separate 5 load free perfume is mixed with Tide® Free unscented granular detergent and added to the wash cycle. The laundered fabrics are dried in conventional driers and stored in loosely sealed aluminum foil bags and odor evaluated over time.

Odor evaluation of the dry fabrics is conducted initially after drying and then again after two weeks. In both cases, the odor of the fabrics treated with the perfume 10 delivery articles is far more intense than the odor observed on fabrics treated with the free perfume. There appears to be a drastic difference between the amount of perfume that is delivered via a perfume delivery article and the amount when free perfume is added to the laundry solution. In addition, it is observed that wet fabrics give the odor of the free perfume, while the dry fabrics give a more intense odor character of the perfume 15 composition entrapped in the zeolite. Analytical evaluation of total perfume delivered onto dry fabrics, in the headspace and physically in the fabric matrix, is tabulated below. The table below indicates a high dry fabric odor intensity initially (in the headspace and on the fabric), and odor longevity (in the headspace and on aged fabrics).

Table D

Method of Perfume Delivery	Headspace of Dry Fabric (nanogram/Liter)	Dry Fabric Deposition (microgram perfume/g fabric)
Perfume Article 1	674.1	79.3
Spray-on Perfume	0.0	31.6
Aged Fabrics with Perfume Article 1	374.8	43.8
Aged Fabrics with Spray-	0.0	0.0

on Perfume		
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The perfume compositions described herein may also be encapsulated in starch, starch derivatives and other hydrating materials for packaging as articles of the present invention.

5

#### EXAMPLE 10

##### *Starch/Starch Derivative Hydrating Materials*

Perfume is added to an approximate 25% modified starch solution with the balance being water. See Table E below. The oil is added to the starch at a rate of about 1g/sec with high agitation. The agitation is provided by an efficient homogenizer to form 10 an emulsion having an oil droplet size of less than about 2 micrometers. The emulsion is then spray dried in a co-current tower having an air inlet temperature of about 200°C and an outlet temperature of about 100°C to yield a dry particle with a mean particle size of about 58 micrometers.

15

**Table E**

<u>Example</u>	<u>(Wt.%)</u>
Perfume	40.2
HICAP 100 -Modified Starch*	57.8
Water	2.0

\* Available from National Starch & Chemical

Once encapsulated, the perfume composition can be incorporated in a variety of article forms such as effervescent articles, non-effervescent articles, foam containing articles, and various other macro-encapsulates.

20

#### EXAMPLE 11

Effervescent articles of the present invention having the composition shown in Table F are prepared by mixing and then compacted the materials in a spherical mold.

Table F

<u>Example</u>	<u>(Wt. %)</u>
Perfume-in-Starch	47.8
Sodium Bicarbonate	32.6
Citric acid	16.3
Propylene glycol	2.2
Canola oil	1.1

5

EXAMPLE 12

Effervescent articles containing cornstarch and witchazel can also be prepared. The articles are prepared by placing the sodium bicarbonate in a common kitchen mixer. The citric acid is added and the mixture is stirred for approximately 5 minutes. The 10 cornstarch is added and the mixture is stirred for about an additional 5 minutes. The mixer is left on while the perfume is titrated into the mixture. Once the addition of perfume is complete, the mixture is stirred for an about additional 10 minutes. Witchhazel is then added to the mixture with stirring until the composition begins to stick 15 together. Doses of the mixture are then placed in a mold and compacted to form spherical articles. The addition of the witchhazel should be monitored closely as addition of an excessive amount of witchhazel is observed to cause the product to effervesce. The components and their order of addition are presented in Table G.

Table G

Component	Order of Addition	Wt. %
Sodium Bicarbonate	1	55.0
Citric acid	2	24.0
Cornstarch	3	17.0
Perfume	4	4.0
Witchhazel	5	Minor

### B. Packaging

The perfume delivery compositions for use in the articles of the present invention will comprise perfume entrapped in zeolite and/or combined with a hydrating material such as effervescing materials. In either case, the stability of the article and its ability to effective release the perfume components requires that such materials be protected from atmospheric moisture with a package having specific moisture barrier characteristics. If exposed to humidity, effervescing components can act as desiccants gradually absorbing moisture that will interfere with the components' ability to effervesce when dispensed in an aqueous solution. Hydration of these powder components is detrimental to the perfume article because deactivation prolongs the dissolution time and may leave residues in the washing machine and/or on fabrics. Further, if there is incomplete dissolution, the perfume carrier material will not be completely released to deposit on the fabric surface such that the benefit delivered will only be a fraction of the target benefit.

In addition, where the perfume is entrapped in a moisture sensitive carrier such as zeolite, the perfume will be desorbed upon adsorption of water, especially water vapor. Water vapor can effectively displace about 95-98% of the perfume entrapped inside the zeolite cavity. More specifically, perfume that has been combined with Zeolite 13X (obtained from UOP) is placed in an open petri dish at about 80°F with about 70% relative humidity. The approximate amount of perfume initially loaded into the zeolite cavities and the approximate amount of perfume lost due to water absorption are tabulated in Table C below.

Table C

Target Loading of perfume in Zeolite X (wt%)	Perfume Oil Loss after 24 hours at 80F/80%RH (open petri dish)
8%	97.6%
12%	96.5%
15%	95.0%

The choice of packaging material for a given hydrating material and/or perfume carrier can be determined by following several steps. First determine the critical amount of water that can be adsorbed or absorbed by the perfume article without losing 5 performance, where the loss of performance can be quantified by the level of perfume components in the headspace above or on the dried fabrics, by the incomplete dissolution of the composition/article, etc. Water absorption may be determined by exposing the composition/article to constant humidity and determining the mass gained over time. Then, evaluate the performance (analytical and/or sensory) of each perfume article to 10 determine the critical quantity of water. Second, determine the surface area of the package in which the perfume articles will be packaged and sold in the trade. Third, determine the in-trade stability requirement, such as the number of months that the finished product is likely to remain in the package prior to use. The maximum moisture vapor transmission rate (MVTR) for the composition/article may be calculated using the 15 following equation:

$$\text{MVTR} = (\text{Critical Mass of Water})/(\text{Surface Area of Package})/(\text{in-trade stability required})$$

[=] g H<sub>2</sub>O/m<sup>2</sup>/day

Tabulated values of MVTR provided in technical references generally report data 20 determined at about 28-38°C, and about 80%-90% relative humidity such that they represent worse case scenario ambient conditions. Selecting the packaging material under these conditions will ensure long term stability of the article.

Preferably, the article is packaged so that moisture penetration must occur through a continuous layer, and the moisture vapor transmission rate of the layer is less than about 25 1.2 g H<sub>2</sub>O/day/m<sup>2</sup>, preferably less than about 0.5 g H<sub>2</sub>O/day/m<sup>2</sup>, more preferably less than

about 0.1 g H<sub>2</sub>O/day/m<sup>2</sup>, even more preferably less than about 0.02 g H<sub>2</sub>O/day/m<sup>2</sup>, and still more preferably 0 g H<sub>2</sub>O/day/m<sup>2</sup>, to ensure article stability.

The packaging selected to ensure minimal perfume oil loss from the zeolite, must meet several requirements. Films that are permeable to water vapor will not be sufficient to ensure stability. Determination of effective packaging materials must be done on a case-by-case basis since perfume materials will have various odor detection thresholds, and performance benefits that may be detected even after about 20-40% of the oil is lost from the zeolite. To ensure long term stability of about 9 to about 12 months in a sealed package, preferred packaging materials will include bimetalized foil materials, glass, and other materials that are capable of providing the described moisture transfer barrier.

10 Preferred foil materials will have about 7 microns of bimetalized film and a MVTR of less than about 0.0155 gH<sub>2</sub>O/m<sup>2</sup>/day.

#### EXAMPLE 13

##### *Package Choice For Spherical Tablets*

15 About 30g of perfume loaded zeolite is mixed with about 57g of a citric acid/sodium carbonate coparticle that has been made by compacting about 31.4g coarse citric acid and about 25.7g fine sodium carbonate at about 100 kN compaction force. Approximately 13g of Polyethylene Glycol 1500 is added to the mixture, under high agitation in a conventional kitchen mixer. The agglomerated powder is tableted using an

20 Instron at about 60 mm/min compression rate, and about 10 kN compaction force, to produce a nominal 18 mm diameter spherical tablet. These tablets are exposed to high humidity conditions and weight gain/loss is monitored during the exposure. Several tablets are added to the wash cycle of an automated washing machine, and the mass of undissolved solids remaining after the wash is monitored.

25 As described above, the deactivation of the effervescent materials due to moisture penetration through a package, typically results in an increase in the undissolved solids in the washing machine. To ensure that no residues remain in the washer, water adsorption by the composition/article must be minimized. For an 18mm diameter spherical tablet whose composition has about 57wt% compacted granules of citric acid and sodium 30 carbonate in a weight ratio of about 1.2, the criteria for no residues in the washing machine is < about 6 mg H<sub>2</sub>O/g product water pickup.

$$MVTR_{\max} = \frac{6 \frac{mgH_2O}{g\_product} \cdot 4.5g\_product}{(30days)(0.008m^2)} = 0.113 \frac{gH_2O}{day \cdot m^2}$$

The nominal 7 microns bimetalлизed film and CycloOlefin clear film materials exceed this MVTR requirement. Compositions and articles stored in these types of packaging materials yielded a high intensity of perfume odor on dried fabrics.

5 Figure 1 is a flow chart illustrating the conversion of raw materials into finished product. The formulation of a rapidly dissolving article often requires the use of moisture sensitive materials. In the preferred embodiment of this invention, the hydrating material is an effervescing material in powder form and the perfume carrier is a water vapor triggered carrier such that both materials deactivate quickly in the presence of high  
10 ambient moisture. Controlled humidity conditions may often be required to prevent premature deactivation.

15 In the preferred embodiment, the performance of processes A, C, E, G, and H require a controlled environment to assure high product quality (rapid solubility, sensory performance, minimum loss of perfume oil). A controlled process environment would consist of temperature and humidity control. Preferably, the temperature is maintained below about 80°C, more preferably below about 50°C, and even more preferably less than about 30°C during these processes. A more critical parameter is the relative humidity in the controlled environment. To ensure minimum deactivation of materials, it is desirable to ensure that the relative humidity is less than about 50%, preferably less than about  
20 40%, and more preferably less than about 30%.

25 Transport steps B and C require package criteria to minimize deactivation during transport. The package criteria can be determined by following the steps outlined above. The package for transporting raw or converted materials can be a big bag (typically 1 cubic meter in volume) available in the industry, with a liner. For the preferred embodiment of the invention, the liner meets a specific MVTR criteria, similar to the MVTR required for article stability.

Preferably, the liner is glued to the outer bag in such a way that moisture penetration must occur through a continuous layer, and the water vapor transmission rate of the layer is less than about 1.2 g H<sub>2</sub>O/day/m<sup>2</sup>, preferably less than about 0.5 g

$\text{H}_2\text{O}/\text{day}/\text{m}^2$ , and more preferably less than about 0.1 g  $\text{H}_2\text{O}/\text{day}/\text{m}^2$ , even more preferably less than about 0.02 g  $\text{H}_2\text{O}/\text{day}/\text{m}^2$ , and still more preferably 0 g  $\text{H}_2\text{O}/\text{day}/\text{m}^2$ , to ensure article stability.

### C. Article Forms and Characteristics

5        Articles that dissolve in water at moderate temperatures are explained extensively in the patent literature concerning detergent tablets. However, there is one serious element lacking in these tablets, namely, the incorporation of a large volume fraction of fines or fine particulate components. Typically, when making tablets with higher fine powder content, excessive amounts of binder must be used which can lead to decreases in  
10      the dissolution rates of the tablet. Often, tablet formulations designed to meet short cycle time solubility criteria have insufficient strength to survive making, packing, transporting, and handling. Thus, it has been a challenge to achieve a spherical tablet that meets strength and solubility criteria, and also is able to incorporate a large volume percentage of a fine powdered perfume carrier, and ensure stability of the article from manufacture to  
15      its end use.

20       The articles of the present invention comprise a temperature and humidity stable unit dose perfume delivery article that comprises a perfume composition, a material selected from a zeolite, a hydrating material and mixtures thereof, and a humidity resistant package, wherein at least about 30%, preferably at least about 40% and more preferably at least about 50% by volume of the components are in the form of fine powders or particulates having a mean particle size of less than about 100 microns, and preferably less than about 40 microns. Further, not only do these articles have sufficient hardness to survive handling, packaging and transportation, but they will rapidly dissolve in water less than about 10°C during a short cycle washing and/or rinsing process without  
25      leaving residue. The articles are preferably tablets that can be dispensed directly into a laundry solution, dispensed to the solution using a washing machine dispenser, or dispensed using a self-contained dispenser such as the Downy Ball®. Once dissolved in solution, the fine particulates deposit perfume components onto the fabric. After the completion of the laundering process, the components provide a slow release of the  
30      perfume components from the dry fabrics when exposed to atmospheric moisture.

The articles of the present invention must be sufficiently strong and robust to withstand all aspects of manufacture, handling, packaging, and transport without breakage. The hardness of various tablets is noted in the several of the examples provided herein. The hardness of an article can be determined using any number of devices and techniques known to those skilled in the art, but were determined herein using a Tablet Hardness Tester, Model TBH 30, commercially available from Copley Scientific (catalog number 082-1510). Preferably the articles of the present invention will have a hardness value of from about 70 Newtons to about 160 Newtons.

Rapid dissolution of the articles is essential for dispensing the perfume composition with the other components to a laundry solution for deposition on fabrics in the solution. This rapid dissolution is essential under both warm and cold water conditions. More specifically, the articles of the present invention will have a dissolution rate that is between 0.5 min and about 15 min in water that is less than about 30°C, preferably between about 0.5 min and about 15 min in water that is less than about 10°C, and more preferably between about 0.5 min and about 3 min. in water that is at about 10°C.

The articles of the present invention, preferably a tablet, preferably weigh less than about 60g, preferably less than about 30g, more preferably less than about 10g, and even more preferably less than about 5g. The tablets can have any size, but when the tablets are to be dispensed in a washing machine or self-contained dispenser, the tablet should be sized accordingly. Specifically, in such a case the tablets will have a diameter that is between about 1 mm and about 30 mm and preferably between about 5 mm and about 26 mm.

The long-term stability of such articles is insured by packaging the articles with materials that provide a moisture barrier, expressed as a moisture vapor transmission rate (MVTR), of less than about 1.2 g H<sub>2</sub>O/day/m<sup>2</sup>, preferably less than about 0.1 g H<sub>2</sub>O/day/m<sup>2</sup>, and more preferably less than about 0.02 g H<sub>2</sub>O/day/m<sup>2</sup>. Packaging that may be used to achieve such transmissions rate is described in detail above.

#### **D. Use and Other Method claims**

The perfume delivery compositions and articles made therefrom may be added to a laundry solution for a simple and effective deposition of the perfume particles on fabric

laundered in those solutions. The use of such compositions and articles provides a more intense dry fabric odor on fabrics laundered in solutions containing them. Not to be bound by theory, but the perfume particles described herein are dispersed in the laundry solution and can then deposit and become entrained in the fibers of the fabrics. After 5 drying and when exposed to atmospheric moisture, moisture vapor displaces the perfume compositions that had been entrapped in the carrier particles. Because the release of the perfume composition is activated more by atmospheric moisture than water, the perfume is mostly retained in the carrier through the laundering process. Further, the mechanism provides for the controlled release of the perfume composition over time, such that the 10 perfume release provides an enduring fragrance that is sufficiently intense for at least 1 week, preferably at least 2 weeks and more preferably at least 3 weeks.

It is also anticipated that the perfume delivery compositions and articles will preferably comprise an optional amount of a free perfume. Although, there are disclosed herein free perfumes that are particularly substantive to fabrics when dispensed in a 15 laundry solution, the primary function of a free perfume herein is to provide an immediately observable "bloom" of a fragrance which may be desirable to meet consumer expectations and desires.

#### **1. Method of selecting a zeolite carrier**

The method of selecting a zeolite perfume carrier is described above both in terms 20 of selecting a type of zeolite that will readily receive and entrap perfume compositions, but also in terms of selecting from amongst a number of zeolites of the same type, namely, one or more preferred type X zeolites. As described in more detail above, it has been found that there are differences zeolites of a given type and that the selection of one 25 or more of those zeolites may be based upon the water content and BET surface area of such zeolites. In the case of X-type zeolites, preferred zeolites will have a total moisture content that is less than about 7wt%, and a BET surface area that is at least about 475 m<sup>2</sup>/g, preferably greater than about 525 m<sup>2</sup>/g, and more preferably greater than about 580 m<sup>2</sup>/g.

#### **2. Method of loading perfume**

30 Generally, but as described above in more detail, the entrapment of the perfume composition in a porous carrier, preferably zeolite, is an exothermic process. By

controlling the heat transfer during the perfume entrapment operation it is possible to manipulate (1) the quantity of perfume adsorbed, (2) the selectivity of perfume molecules adsorbed into the cavity, and (3) the retention of the adsorbed perfume molecules through a laundering process. The carrier is first contacted with the perfume composition. As the 5 perfume composition becomes entrapped in the pores of the carrier, heat is generated. The objective is to allow the mixture of carrier and perfume composition to heat to a pre-determined temperature before controlling the heat transfer through the cooling of the mixture.

#### ANALYTICAL METHODS

10 **After simulated wash method**

Prepare detergent solution by adding about 1.03 grams of Tide® Free granular detergent to a 1000 milliliter volumetric flask and filling to mark with deionized water. A stir bar is added and the solution stirred gently until dissolved. The solution is filtered through a 5 micron nylon filter using a 47 mm filter holder designed for vacuum filtering of particulates from liquids. The solution is filtered a second time using a 0.45 mm nylon filter. Heat the filtrate at about 32°C for about 1 hour in a water bath. Weigh out about 15 80 to 100 mg of the sample and add about 20 ml of filtered detergent solution and mix for about 5 minutes. Filter with a 0.45 mm nylon filter and rinse with about 20 ml of water. Remove filter and place in a 20 ml scintillation vial and run total perfume extraction method.

20 **Total perfume extraction method**

Weigh out about 20 - 30 g of zeolite, add about 200 microliters of water, about 25 200 microliters of acetone, and about 100 microliters of internal standard solution. Mix well, add about 9.5 ml of acetone and mix again. Place in water bath at about 60°C for about 1 hour. Remove from water bath and allow the solution to cool to room temperature. Attach a 10 ml syringe to a 0.5 micron Millex-LCR filter. Transfer contents of scintillation vial into syringe and filter into a clean scintillation vial. Transfer the filtrate into an autosampler vial and analyze on GC/FID (Gas Chromatography/Flame Ionization Detector).

30 **Determination of Dry Fabric Odor:**

Perfume with zeolite or perfume articles are evaluated for fabric odor performance

by adding them to a wash and/or rinse cycle during a normal laundering process. Cotton test terries are placed in a washing machine along with other typical clothing to make up about a nominal 7 lb. load. Tide® Free unscented powder detergent is added at the recommended level for a normal size load containing about 17 gallons of water. The test product is added and warm water is used during a normal wash cycle using a typical vertical axis US washing machine. The wash cycle is followed by a cold rinse cycle. Alternatively, test product is added at the start of the rinse cycle.

The test terries are machine dried on a cotton high temperature setting until they are dry. The test terries are evaluated by an expert perfumer for dry fabric odor intensity.

Test terries are evaluated initially after being removed from the dryer for about 1-2 hours and may be re-evaluated periodically for several weeks.

**What is claimed is:**

1. A laundry additive composition for dispensing in a laundry wash and/or rinse bath, the composition comprising a
  - a. hydrating material that is between about 0% and about 90%, is preferably between about 30% and 60% by weight of the composition, and even more preferably between about 50% and 60% by weight of the composition;
  - b. perfume particles having carrier particles and a perfume composition; and
  - c. optionally, one or more of a compatible binder material, free perfume, colorant, and disintegrants.
2. The composition of claim 1, wherein the carrier particles have an average particle size of less than about 100 microns and preferably less than about 40 microns.
3. The composition of any one of claims 1-2, wherein the carrier particles comprise between about 1% and about 40% and preferably between about 20% and about 30% by weight of the composition.
4. The composition of any one of claims 1-3, wherein the binding material is present between about 5% and about 20% and preferably between about 10% and about 15% by weight of the composition.
5. The composition of any one of claims 1-4, wherein the binder has a softening temperature in the range of about 35° to about 100°C and preferably between about 35° and about 65° C.
6. The composition of any one of claims 1-5, wherein the binder has a free water content less than about 10% by weight of the composition, said binder dissolving less than about 5wt% of the perfume active and preferably less than 3wt%.

7. The composition of any one of claims 1-6, wherein the binder is selected from the group consisting of ethoxylated diamines, glucose, sorbitol, glycerin, polyethylene glycols, polyols, modified starches, and modified starch derivatives, and mixtures thereof.
8. The composition of any one of claims 1-7, wherein the hydrating material is an effervescing composition comprising particulate acid and carbon dioxide source material.
9. The composition of claim 8, wherein particulate acid comprise citric acid particles having a mean particle size between about 0.1 microns and about 1180 microns, preferably between about 300 microns and 700 microns.
10. The composition of claim 8, wherein the carbon dioxide source material are carbonate particles have a mean particle size of less than about 100 microns, preferably less than about 38 micrometers, and even more preferably less than about 10 microns.
11. The composition of claim 8, wherein the ratio of particulate acid to carbon dioxide source material is from about 0.05 to about 3, preferably from about 0.1 to about 1.5, and more preferably from about 0.2 to about 1.0.
12. The composition of any one of claims 1-11, wherein the carrier particles are a silica, clay, starch, starch derivative, sugar, sugar derivative, zeolite, or mixture thereof.
13. The composition of claim 1, 3-12 wherein the carrier particle is zeolite X, zeolite Y, or mixtures thereof, said carrier particles having a mean particle size between about 0.1 microns and about 250 microns, preferably less than about 100 microns, more preferably less than about 30 microns and even more preferably less than about 5 microns.
14. The composition of any one of claims 1-13, wherein the perfume composition is at least about 1%, more preferably at least about 3%, and even more preferably at least about 5% by weight of the composition.

15. The composition of any one of claims 1-14, wherein the perfume composition and/or free perfume comprises a perfume active or mixture of perfume actives selected from the group consisting of aromatic and aliphatic esters having molecular weights from about 130 to about 250; aliphatic and aromatic alcohols having molecular weights from about 90 to about 240; aliphatic ketones having molecular weights from about 150 to about 260; aromatic ketones having molecular weights from about 150 to about 270; aromatic and aliphatic lactones having molecular weights from about 130 to about 290; aliphatic aldehydes having molecular weights from about 140 to about 200; aromatic aldehydes having molecular weights from about 90 to about 230; aliphatic and aromatic ethers having molecular weights from about 150 to about 270; and condensation products of aldehydes and amines having molecular weights from about 180 to about 320 and mixtures thereof.
16. The composition of claim 15, wherein the free perfume comprises a perfume active or mixture of actives that is at least about 25%, more preferably about 50%, and even more preferably about 75%, by weight of the perfume composition, of perfume ingredients with a ClogP equal or greater than about 2.7, preferably equal or greater than about 2.9, more preferably equal or greater than about 3.0, and a boiling point of about 240°C or higher, and preferably of about 250°C or higher.
17. The composition of claim 16, wherein said perfume composition comprises a perfume active or mixture of perfume actives selected from the group consisting of benzyl salicylate, adoxal, allyl cyclohexane propionate, alpha damascone, oxacycloheptadec-10-en-2-one, 5-cyclohexadecen-1-one, ambroxan, amyl cinnamic aldehyde, amyl cinnamic aldehyde dimethyl acetal, amyl salicylate, 2,5,5-trimethyl-octahydro-2-naphthol, 7-acetyl-1,2,3,4,5,6,7,8-octahydro-1,1,6,7,tetramethylnaphthalene, 2-ethyl-4-(2,2,3-trimethyl-3-cyclopenten-1-yl)-2-buten-1-ol, hydroxycitronellal-methyl anthranilate, benzyl benzoate, 3,3-dimethyl-5-(2,2,3 trimethyl-3-cyclopenten-1-yl)-4-penten-2-ol, undecalactone, beta naphthol methyl ether, 3-(4-tert butylphenyl)-propanal, cyclohexadecenone, caryophyllene, methyl cedrylone, 1-(5,5-dimethyl-1-cyclohexen-1-yl)- 4-penten-1-one, cedramber, cedrynyl acetate, cedrol, ethylene dodecane dioate, cis-3-hexenyl salicylate, citrathal, citronellyl propionate, 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-

hexamethylcyclopenta-gamma-2-benzopyrane, cyclohexyl salicylate, 2-methyl-3-(para iso propyl phenyl)propionaldehyde, beta damascone, delta damascone, 1-(2,6,6-trimethyl-1,3-cyclohexadien-1-yl)-2-buten-1-one, dihydro iso jasmonate, diphenyl methane, 4-(tricyclo(5.2.1.0 2,6)decylidene-8)-butanal, diphenyl oxide, gamma-dodecalactone, delta-dodecalactone, ethyl cinnamate, ebanol, ethylene brassylate, 3-(3-isopropylphenyl) butanol, oxacyclohexadec-12+13-en-2-one, hexyl cinnamic aldehyde, hexyl salicylate, 2-cyclododecyl-propanol, alpha ionone, beta ionone, gamma methyl ionone, methyl ionone, iralia, iso butyl quinoline, lauric aldehyde, 2-methyl-3(para tertbutylphenyl) propionaldehyde, musk ketone, 4-acetyl-6-tert butyl-1,1-dimethyl indane, 7-acetyl-1,1,3,4,4,6-hexamethyl tetralin, 1,2,3,4,4a,5,8,8a-octahydro-2,2,6,8-tetramethyl-1-naphthalenol, tridecen-2-nitrile, 5-acetyl-1,1,2,3,3,6-hexamethylindan, cyclohexyl phenyl ethyl ether, phenyl ethyl benzoate, 2-phenylethyl phenyl acetate, vetiveryl acetate, sandalwood, amyl benzoate, amyl cinnamate, cadinene, cedryl acetate, cedryl formate, cinnamyl cinnamate, cyclamen aldehyde, 15-hydroxypentadecanoic acid lactone), geranyl anthranilate, hexadecanolide, hexenyl salicylate, linalyl benzoate, 2-methoxy naphthalene, methyl cinnamate, methyl dihydrojasmonate, beta-methyl napthyl ketone, musk tibetine, myristicin, delta-nonalactone, oxahexadecanolide-10, oxahexadecanolide-11, patchouli alcohol, phenyl heptanol, phenyl hexanol, alpha-santalol, delta-undecalactone, gamma-undecalactone, yara-yara, methyl-N-methyl anthranilate, benzyl butyrate, benzyl iso valerate, citronellyl isobutyrate, delta nonalactone, dimethyl benzyl carbonyl acetate, dodecanal, geranyl acetate, geranyl isobutyrate, gamma-ionone, para-isopropyl phenylacetaldehyde, 7-acetyl-1,1,3,4,4,6-hexamethyl tetralin, iso-amyl salicylate, ethyl undecylenate, benzophenone, beta-caryophyllene, dodecalactone, para-tertiary-butyl-alpha-methyl hydrocinnamic aldehyde, and mixtures thereof.

18. The composition of claim 15, wherein the perfume composition comprises a perfume active that is at least about 25%, more preferably about 50%, and even more preferably about 75%, by weight of the perfume composition, of perfume ingredients with a ClogP equal or less than about 3.0, preferably equal or less than about 2.9, more preferably equal or less than about 2.7, and a boiling point of about 250°C or lower, and preferably of about 240°C or lower.

19. The composition of claim 18, wherein the active is a perfume or mixture of perfume actives selected from the group consisting of allyl amyl glycolate, 1,5,5,9-tetramethyl-1,3-oxatricyclotridecane, anethole, 2-ethyl-4-(2,2,3-trimethyl-3-cyclopenten-1-yl)-2-buten-1-ol, benzyl acetone, benzyl salicylate, butyl anthranilate, calone, dodecahydro-3A,6,6,9A-tetramethylnaphtho[2,1B]-furan, cinnamic alcohol, coumarin, cyclogalbanate, 3,5-dimethyl-3-cyclohexene-1-carboxaldehyde, 2-methyl-3-(para iso propylphenyl)propionaldehyde, 1-(2,6,6-trimethyl-1,3-cyclohexadien-1-yl)-2-buten-1-one, alpha-damascone, 4-decenal, dihydro isojasmonate, gamma-dodecalactone, ebanol, ethyl anthranilate, ethyl-2-methyl butyrate, ethyl methylphenyl glycidate, ethyl vanillin, eugenol, dihydro-nor-cyclopentadienyl acetate, 3-(3-isopropylphenyl) butanol, ethyl-2-methyl-1,3-dioxolane-2-acetate), dihydro-nor-cyclopentadienyl propionate, heliotropin, herbavert, cis-3-hexenyl salicylate, indole, alpha ionone, beta ionone , iso cyclo citral, isoeugenol, alpha-isomethylionone, keone, para-tertiary butyl alpha-methyl hydrocinnamic aldehyde, linalool, lyrat, methyl anthranilate, methyl dihydrojasmonate, methyl heptine carbonate, methyl isobutetyl tetrahydropyran, methyl beta naphthyl ketone, methyl nonyl ketone, beta naphthol methyl ether, nerol, para-anisic aldehyde, para hydroxy phenyl butanone, phenyl acetaldehyde, gamma-undecalactone, undecylenic aldehyde, vanillin, and mixtures thereof.
20. The composition of Claim 1, wherein said perfume composition comprises less than about 30%, preferably less than about 15%, more preferably less than about 8%, even more preferably less than about 6%, and yet even more preferably less than about 3%, by weight of the perfume composition, of unstable perfume ingredients.
21. The perfume composition of Claim 20, wherein said unstable perfume ingredient is selected from the group consisting of allylic alcohol ester, secondary alcohol ester, tertiary alcohol ester, allylic ketone, acetal, ketal, condensation product of amines and aldehydes, and mixtures thereof.
22. The composition of Claim 21, wherein said allylic alcohol ester is selected from the group consisting of allyl amyl glycolate, allyl anthranilate, allyl

benzoate, allyl butyrate, allyl caprate, allyl caproate, allyl cinnamate, allyl cyclohexane acetate, allyl cyclohexane butyrate, allyl cyclohexane propionate, allyl heptoate, allyl nonanoate, allyl salicylate, amyl cinnamyl acetate, amyl cinnamyl formate, cinnamyl formate, cinnamyl acetate, cyclogalbanate, geranyl acetate, geranyl acetoacetate, geranyl benzoate, geranyl cinnamate, methallyl butyrate, methallyl caproate, neryl acetate, neryl butyrate, amyl cinnamyl formate, alpha-methyl cinnamyl acetate, methyl geranyl tiglate, mertenyl acetate, farnesyl acetate, fenchyl acetate, geranyl anthranilate, geranyl butyrate, geranyl iso-butyrate, geranyl caproate, geranyl caprylate, geranyl ethyl carbonate, geranyl formate, geranyl furoate, geranyl heptoate, geranyl methoxy acetate, geranyl pelargonate, geranyl phenylacetate, geranyl phthalate, geranyl propionate, geranyl iso-propoxyacetate, geranyl valerate, geranyl iso-valerate, trans-2-hexenyl acetate, trans-2-hexenyl butyrate, trans-2-hexenyl caproate, trans-2-hexenyl phenylacetate, trans-2-hexenyl propionate, trans-2-hexenyl tiglate, trans-2-hexenyl valerate, beta-pentenyl acetate, alpha-phenyl allyl acetate, prenyl acetate, trichloromethylphenylcarbonyl acetate, amyl vinyl carbonyl acetate, amyl vinyl carbonyl propionate, hexyl vinyl carbonyl acetate, 3-nonenyl acetate, 4-hydroxy-2-hexenyl acetate, linallyl anthranilate, linallyl benzoate, linallyl butyrate, linallyl isobutyrate, linallyl caproate, linallyl caprylate, linallyl cinnamate, linallyl citronellate, linallyl formate, linallyl heptoate, linallyl-N-methylanthranilate, linallyl methyltiglate, linallyl pelargonate, linallyl phenylacetate, linallyl propionate, linallyl pyruvate, linallyl salicylate, linallyl-n-valerate, linallyl-iso-valerate, myrtenyl acetate, nerolidyl acetate, nerolidyl butyrate, beta-pentenyl acetate, alpha-phenyl allyl acetate, and mixtures thereof; wherein said secondary alcohol ester is selected from the group consisting of secondary-n-amyl acetate, ortho-tertiary-amyl cyclohexyl acetate, isoamyl benzyl acetate, secondary-n-amyl butyrate, amyl vinyl carbonyl acetate, amyl vinyl carbonyl propionate, cyclohexyl salicylate, dihydro-nor-cyclopentadienyl acetate, dihydro-nor-cyclopentadienyl propionate, isobornyl acetate, isobornyl salicylate, isobornyl valerate, flor acetate, frutene, 2-methylbuten-2-ol-4-acetate, methyl phenyl carbonyl acetate, 2-methyl-3-phenyl propan-2-yl acetate, prenyl acetate, 4-tert-butyl cyclohexyl acetate, 2-tert-butyl cyclohexyl acetate, 4-tert-butylcyclohexyl acetate, carbonic acid 4-cycloocten-1-yl methyl ester, ethenyl-iso-amyl carbonylacetate, fenchyl acetate, fenchyl benzoate, fenchyl-n-butyrate, fenchyl

isobutyrate, laevo-menthyl acetate, dl-menthyl acetate, menthyl anthranilate, menthyl benzoate, menthyl-iso-butyrate, menthyl formate, laevo-menthyl phenylacetate, menthyl propionate, menthyl salicylate, menthyl-iso-valerate, cyclohexyl acetate, cyclohexyl anthranilate, cyclohexyl benzoate, cyclohexyl butyrate, cyclohexyl-iso-butyrate, cyclohexyl caproate, cyclohexyl cinnamate, cyclohexyl formate, cyclohexyl heptoate, cyclohexyl oxalate, cyclohexyl pelargonate, cyclohexyl phenylacetate, cyclohexyl propionate, cyclohexyl thioglycolate, cyclohexyl valerate, cyclohexyl-iso-valerate, methyl amylacetate, methyl benzyl carbonyl acetate, methyl butyl cyclohexanyl acetate, 5-methyl-3-butyl-tetrahydropyran-4-yl acetate, methyl citrate, methyl-iso-campholate, 2-methyl cyclohexyl acetate, 4-methyl cyclohexyl acetate, 4-methyl cyclohexyl methyl carbonyl acetate, methyl ethyl benzyl carbonyl acetate, 2-methylheptanol-6-acetate, methyl heptenyl acetate, alpha-methyl-n-hexyl carbonyl formate, methyl-2-methylbutyrate, methyl nonyl carbonyl acetate, methyl phenyl carbonyl acetate, methyl phenyl carbonyl anthranilate, methyl phenyl carbonyl benzoate, methyl phenyl carbonyl-n-butyrate, methyl phenyl carbonyl-iso-butyrate, methyl phenyl carbonyl caproate, methyl phenyl carbonyl caprylate, methyl phenyl carbonyl cinnamate, methyl phenyl carbonyl formate, methyl phenyl carbonyl phenylacetate, methyl phenyl carbonyl propionate, methyl phenyl carbonyl salicylate, methyl phenyl carbonyl-iso-valerate, 3-nonanyl acetate, 3-nonenyl acetate, nonane diol-2:3-acetate, nonynol acetate, 2-octanyl acetate, 3-octanyl acetate, n-octyl acetate, secondary-octyl-iso-butyrate, beta-pentenyl acetate, alpha-phenyl allyl acetate, phenylethyl methyl carbonyl-iso-valerate, phenylethyleneglycol diphenylacetate, phenylethyl ethyl carbonyl acetate, phenylglycol diacetate, secondary-phenylglycol monoacetate, phenylglycol monobenzoate, isopropyl caprate, isopropyl caproate, isopropyl caprylate, isopropyl cinnamate, para-isopropyl cyclohexanyl acetate, propylglycol diacetate, propyleneglycol diisobutyrate, propyleneglycol dipropionate, isopropyl-n-heptoate, isopropyl-n-hept-1-yne carbonate, isopropyl pelargonate, isopropyl propionate, isopropyl undecylenate, isopropyl-n-valerate, isopropyl-n-valerate, isopropyl-iso-valerate, isopropyl sebacinate, isopulegyl acetate, isopulegyl acetoacetate, isopulegyl isobutyrate, isopulegyl formate, thymyl propionate, alpha-2,4-trimethyl cyclohexane methylacetate, trimethyl cyclohexyl acetate, vanillin triacetate, vanillylidene diacetate, vanillyl vanillate, and mixtures thereof; wherein said tertiary alcohol ester is selected from the group consisting of

tertiary-amyl acetate, caryophyllene acetate, cedrenyl acetate, cedryl acetate, dihydromyrcenyl acetate, dihydroterpinyl acetate, dimethyl benzyl carbinal acetate, dimethyl benzyl carbinal isobutyrate, dimethyl heptenyl acetate, dimethyl heptenyl formate, dimethyl heptenyl propionate, dimethyl heptenyl-iso-butyrate, dimethyl phenylethyl carbinal acetate, dimethyl phenylethyl carbinal-iso-butyrate, dimethyl phenylethyl carbinal-iso-valerate, dihydro-nor-dicyclopentadienyl acetate, dimethyl benzyl carbinal butyrate, dimethyl benzyl carbinal formate, dimethyl benzyl carbinal propionate, dimethyl phenylethyl carbinal-n-butyrate, dimethyl phenylethyl carbinal formate, dimethyl phenylethyl carbinal propionate, elemyl acetate, ethinyl cyclohexylacetate, eudesmyl acetate, eugenyl cinnamate, eugenyl formate, iso-eugenyl formate, eugenyl phenylacetate, isoeudehyl phenylacetate, guaiyl acetate, hydroxycitronellyl ethylcarbonate, linallyl acetate, linallyl anthranilate, linallyl benzoate, linallyl butyrate, linallyl isobutyrate, linallyl carproate, linallyl caprylate, linallyl cinnamate, linallyl citronellate, linallyl formate, linallyl heptoate, linallyl-N-methylanthranilate, linallyl methyltiglate, linallyl pelargonate, linallyl phenylacetate, linallyl propionate, linallyl pyruvate, linallyl salicylate, linallyl-n-valerate, linallyl-iso-valerate, methylcyclopentenolone butyrate, methyl cyclopentenolone propionate, methyl ethyl phenyl carbinal acetate, methyl heptin carbonate, methyl nicotinate, myrcenyl acetate, myrcenyl formate, myrcenyl propionate, cis-ocimanyl acetate, phenyl salicylate, terpinyl acetate, terpinyl anthranilate, terpinyl benzoate, terpinyl-n-butyrate, terpinyl-iso-butyrate, terpinyl cinnamate, terpinyl formate, terpinyl phenylacetate, terpinyl propionate, terpinyl-n-valerate, terpinyl-iso-valerate, tributyl acetylcitrate, , and mixtures thereof; wherein said allylic ketone is selected from the group consisting of acetyl furan, allethrolone, allyl ionone, allyl pulegone, amyl cyclopentenone, benzylidene acetone, benzylidene acetophenone, alpha iso methyl ionone, 4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3-buten-2-one, beta damascone (1-(2,6,6-trimethylcyclohexen-1-yl)-2-buten-1-one), damascenone (1-(2,6,6-trimethyl-1,3-cyclohexadien-1-yl)-2-buten-1-one), delta damascone (1-(2,6,6-trimethyl-3-cyclohexen-1-yl)-2-buten-1-one), alpha ionone (4-(2,6,6-trimethyl-1-cyclohexenyl-1-yl)-3-buten-2-one), beta ionone (4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3-butene-2-one), gamma methyl ionone (4-(2,6,6-trimethyl-2-cyclohexyl-1-yl)-3-methyl-3-buten-2-one), pulegone, and mixtures thereof; wherein said acetal is selected from the group consisting of acetaldehyde-

benzyl-beta-methoxyethyl acetal, acetaldehyde-di-iso-amyl acetal, acetaldehyde-di-pentandiol acetal, acetaldehyde-di-n-propyl acetal, 10 acetaldehyde-ethyl-trans-3-hexenyl acetal, acetaldehyde-phenylethylene glycol acetal, acetaldehyde phenylethyl-n-propyl acetal, cinnamic aldehyde dimethyl acetal, acetaldehyde-benzyl-beta-methoxyethyl acetal, acetaldehyde-di-iso-amyl acetal, acetaldehyde diethyl acetal, acetaldehyde-di-cis-3-hexenyl acetal, acetaldehyde-di pentanediol acetal, acetaldehyde-di-n-propyl acetal, acetaldehyde-ethyl-trans-3-hexenyl acetal, acetaldehyde-phenylethylene glycol acetal, acetaldehyde phenylethyl-n-propyl acetal, acetylvanillin dimethyl acetal, alpha-amylcinnamic aldehyde-di-iso-propyl acetal, p-tertiary-amyl phenoxy acetaldehyde diethyl acetal, anisaldehyde-diethyl acetal, anisaldehyde-dimethyl acetal, iso-apiole, benzaldehyde diethyl acetal, benzaldehyde-di-(ethylene glycol monobutylether) acetal, benzaldehyde dimethyl acetal, benzaldehyde ethylene glycol acetal, benzaldehyde glycetyl acetal, benzaldehyde propylene glycol acetal, cinnamic aldehyde diethyl acetal, citral diethyl acetal, citral dimethyl acetal, citral propylene glycol acetal, alpha-methylcinnamic aldehyde diethyl acetal, alpha-cinnamic aldehyde dimethyl acetal, phenylacetaldehyde-2,3-butenyl acetal, phenylacetaldehyde citronellyl methyl acetal, phenylacetaldehyde diallyl acetal, phenylacetaldehyde diethyl acetal, phenylacetaldehyde dibenzyl acetal, phenylacetaldehyde dibutyl acetal, phenylacetaldehyde diethyl acetal, phenylacetaldehyde digeranyl acetal, phenylacetaldehyde dimethyl acetal, phenylacetaldehyde ethylene glycol acetal, phenylacetaldehyde glycetyl acetal, citronellal cyclomonoglycol acetal, citronellal diethyl acetal, citronellal dimethyl acetal, citronellal diphenylethyl acetal, geranoxyacetaldehyde diethyl acetal, and mixtures thereof; wherein said ketal is selected from the group consisting of acetone diethylketal, acetone dimethylketal, acetophenone diethyl ketal, methyl amyl catechol ketal, methyl butyl catechol ketal, and mixtures thereof; and wherein said condensation product of amine and aldehyde is selected from the group consisting of anisaldehyde-methylanthranilate, hydroxycitronellal methylanthranilate, 4-tert-butyl-alpha-methyldihydrocinnamaldehyde methyl anthranilate, 2,4-dimethyl-3-cyclohexene carbaldehyde, hydroxycitronellal ethylanthranilate, hydroxycitronellal linallylanthranilate, methyl-N-(4-(4-hydroxy-4-methylpentyl)-3-cyclohexenyl-methylidene)-anthranilate, methyl naphthylketone-methylanthranilate, methyl nonyl acetaldehyde

methylanthranilate, methyl-N-(3,5,5-trimethylhexylidene) anthranilate, vanillin methylanthranilate, and mixtures thereof.

23. The composition of Claim 1, wherein said perfume comprises at least about 70%, preferably at least about 85%, more preferably at least about 93%, even more preferably at least about 95%, yet even more preferably at least about 97%, and even more preferably at least about 99%, by weight of the perfume composition, of stable perfume ingredients.
24. The composition of Claim 1, wherein said perfume composition comprises at least about 6 perfume ingredients, preferably at least about 7 perfume ingredients, more preferably at least about 8 perfume ingredients, even more preferably at least 9 perfume ingredients, and most preferably at least about 10 perfume ingredients.
25. The composition according to claim 1, further comprising a fabric care active selected from the group consisting of bodying agents, drape and form control agents, smoothness agents, static control agents, wrinkle control agents, sanitization agents, drying agents, stain resistance agents, soil release agents, malodor control agents, dye fixatives, dye transfer inhibitors, color maintenance agents, anti-fading agents, whiteness enhancers, anti-abrasion agents, fabric integrity agents, anti-wear agents, defoamers and anti-foaming agents, rinse aids, UV protection agents, sun fade inhibitors, insect repellents, enzymes, and mixtures thereof.
26. The composition of claim 25, wherein the fabric care active is an organic compound having a ClogP of at least about 3, or a mixture of organic compounds wherein at least about 25%, preferably about 50% and more preferably about 75% by weight of the perfume composition, are compounds having a ClogP of at least about 3.
27. A laundry additive article for dispensing in a laundry wash and/or rinse bath, the article comprising
  - A. a perfume composition; and
  - a material selected from the group comprising zeolites, hydrating materials and mixtures thereof; and

B. a humidity resistant package;  
wherein at least about 30%, preferably at least about 40% and more preferably at least about 50% by volume of the components are in the form of fine particulates having a mean particle size of less than about 100 microns, and preferably less than about 40 microns

28. The article of claim 27, wherein said perfume composition comprises less than about 30%, preferably less than about 15%, more preferably less than about 8%, even more preferably less than about 6%, and yet even more preferably less than about 3%, by weight of the perfume composition, of unstable perfume ingredients.

29. The article of any one of claims 27-28, wherein the package has a water vapor transmission rate of less than about 1.2 g H<sub>2</sub>O/day/m<sup>2</sup>, preferably less than about 0.5 g H<sub>2</sub>O/day/m<sup>2</sup>, more preferably less than about 0.1 g H<sub>2</sub>O/day/m<sup>2</sup>, even more preferably less than about 0.02 g H<sub>2</sub>O/day/m<sup>2</sup> and still more preferably 0 g H<sub>2</sub>O/day/m<sup>2</sup>.

30. The article of any one of claims 27-29, wherein said package is a film.

31. The article of any one of claims 30, wherein the film provides a continuous layer moisture barrier.

32. The article of any one of claims 27-31, wherein the composition has a dissolution rate between about 0.5 and about 15 minutes in an aqueous solution at less than about 30°C.

33. The article of any one of claims 27-31, wherein the composition has a dissolution rate between about 0.5 and about 15 minutes in an aqueous solution at less than about 10°C.

34. The article of claim 33, wherein the composition has a dissolution rate between about 0.5 and about 3 minutes in an aqueous solution at less than about 10°C.

35. The article of any one of claims 28-34, wherein the A. components are in the form of a tablet.
36. The article of any one of claims 28-35, further comprising a water soluble dye.
37. The article of claim 35, wherein the tablet has a hardness value from about 70 Newtons to about 160 Newtons.
38. The article of claim 35, wherein the weight of the article is less than about 30g, preferably less than about 10g, and even more preferably less than about 5g.
39. The article of claim 35, wherein the tablet has a diameter between about 1 mm and about 30mm and preferably between about 5 mm and about 26 mm.
40. The article of any one of claims 27-39, wherein the free water content is less than 5% by weight of the article.
41. A process for preparing a laundry additive article comprising a hydrating material, carrier particles and a compatible binder, the process comprising the steps of:
  - a) preparing a mixture of a carrier particles and hydrating material;
  - b) heating and adding the compatible binder to the prepared mixture;
  - c) separating particles having a size between about 75 microns and about 850 microns; and
  - d) forming articles from the separated particles;wherein humidity conditions are controlled during steps a) through d) to prevent deactivation of the hydrating material and/or carrier particles, said humidity being maintained below about 50%RH, preferably below about 30%RH, more preferably below about 20%RH, at a temperature of 25°C.
42. The process of claim 41, wherein the hydrating material is converted using compacting and grinding techniques.

43. The process of claim 42, wherein the hydrating material is compacted with a roller compactor using a compaction force of between 60-120 kN and then ground into a particulate.
44. The use of a composition according to any one of claims 1-26 to provide improved deposition and controlled release of perfume from fabric.
45. The use of an article according to any one of claims 27-40 to provide improved deposition and controlled release of perfume from fabric.
46. A method for obtaining a controlled release of perfume from fabric, the method comprising the step of depositing a composition according to any one of claims 1-26 on said fabric.
47. The method of claim 46, wherein the composition is dispensed into an aqueous laundry solution and the fabrics are contacted with the solution.
48. The method of claim 46, wherein the composition is in the form of an article according to any one of claims 27-40.
49. A composition for delivering perfume to fabrics, the composition comprising:
  - a. porous zeolite particles, said particles having a mean surface area of between about 475 m<sup>2</sup>/g and about 600 m<sup>2</sup>/g, preferably between about 525 m<sup>2</sup>/g and about 590 m<sup>2</sup>/g, and even more preferably between about 575 m<sup>2</sup>/g and about 585 m<sup>2</sup>/g; and
  - b. a perfume composition loaded into the pores of the zeolite; wherein when the composition is deposited on fabric in an aqueous solution, at least 60% of the perfume, preferably at least 75% and more preferably at least 90% is retained in the pores of the zeolite particles.
50. The composition of Claim 49, wherein said perfume composition comprises less than about 30%, preferably less than about 15%, more preferably less than about 8%, even more preferably less than about 6%, and yet even more preferably less than about 3%, by weight of the perfume composition, of unstable perfume ingredients.

51. A method of combining a perfume with a porous zeolite for deposition on fabrics to provide an enduring dry fabric odor, the method comprising the steps of:
  - selecting a zeolite, said zeolite having particles that have a mean surface area of at least  $475\text{m}^2/\text{g}$ , preferably greater than  $525\text{ m}^2/\text{g}$  and more preferably greater than  $580\text{m}^2/\text{g}$ ; and
  - mixing the perfume and zeolite.
52. The method of claim 51, wherein the zeolite is preferably a zeolite X.
53. A method of entrapping a perfume composition in a porous zeolite for subsequent deposition on fabrics to provide an enduring dry fabric odor to the fabrics, wherein the entrapment of the perfume composition in the pores of the zeolite is exothermic, the method comprising the steps of:
  - combining the zeolite with the perfume composition;
  - allowing the combined zeolite and perfume composition to generate heat;
  - and
  - cooling the heated zeolite and perfume composition.
54. The method of Claim 53, wherein said perfume composition comprises less than about 30%, preferably less than about 15%, more preferably less than about 8%, even more preferably less than about 6%, and yet even more preferably less than about 3%, by weight of the perfume composition, of unstable perfume ingredients.
55. The method of claim 54, further comprising the step of pre-determining the amount of heat that the perfume and zeolite should generate before cooling the zeolite and perfume composition.

## INTERNATIONAL SEARCH REPORT

In      International Application No  
PCT/US 02/13812A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7    C11D3/50    C11D17/04

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7    C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 955 419 A (BARKET JR DENNIS JOSEPH ET AL) 21 September 1999 (1999-09-21)  claims; example 1	1,3, 12-23, 25,44, 49,51-54
X	US 5 858 959 A (SURUTZIDIS ATHANASIOS ET AL) 12 January 1999 (1999-01-12)  claims	1-7, 12-25, 44,49
X	WO 97 34981 A (PROCTER & GAMBLE (US)) 25 September 1997 (1997-09-25) page 11, line 18 - line 37; claims	1,12-23, 44
X	EP 0 816 484 A (GIVAUDAN ROURE INT) 7 January 1998 (1998-01-07)  claims; example 1	1,3,5-7, 12-14
		-/-

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

## \* Special categories of cited documents :

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Date of the actual completion of the International search

Date of mailing of the International search report

5 August 2002

13/08/2002

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## INTERNATIONAL SEARCH REPORT

In  National Application No  
PCT/US 02/13812

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